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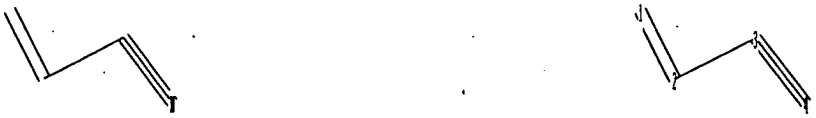

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Match level :
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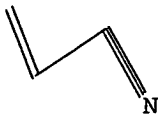
L1 STR



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FULL SCREEN SEARCH COMPLETED -   316533 TO ITERATE

100.0% PROCESSED   316533 ITERATIONS                    266058 ANSWERS
SEARCH TIME: 00.00.03

L2       266058 SEA SSS FUL L1

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                                                 ENTRY    SESSION
FULL ESTIMATED COST                             172.10     172.31

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=> s l2 and hydrogen? and (alcohol? or ?anol? or ?ahol? or ?polyol?)
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        444412 ALCOHOL?
        591755 ALC
        194903 ALCS
        690853 ALC
                 (ALC OR ALCS)
        871250 ALCOHOL?
                 (ALCOHOL? OR ALC)
       1015420 ?ANOL?
           296 ?AHOL?
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        926359 ?AMIDE?
       1736980 ?AMINE?
L4         372 L3 AND CATALYST AND (?ETHER? OR ?AMIDE? OR ?AMINE?)
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=> s l4 and hydrogenation
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          2313 HYDROGENATIONS
        176825 HYDROGENATION
                 (HYDROGENATION OR HYDROGENATIONS)
L5         139 L4 AND HYDROGENATION

=> d l5 125-139 ibib abs hitstr
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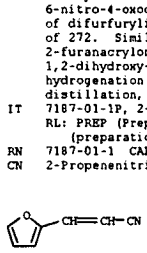
L5 ANSWER 125 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1955:23851 CAPLUS
DOCUMENT NUMBER: 49:23851
ORIGINAL REFERENCE NO.: 49:4618c-e
TITLE: Synthesis of a polyamide from furfural. II. Experiments on the ring cleavage of the furylidene system
AUTHOR(S): Okawara, Makoto
CORPORATE SOURCE: Naniwa Univ., Sakai
SOURCE: Kogyo Kagaku Zasshi (1953), 56, 90-2
CODEN: KGKZA7; ISSN: 0368-5462
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. C.A. 47, 4832h. The compds. having the grouping 2-(2-furyl)vinyl or 2-(2-furyl)-2-hydroxyethyl were synthesized and heated with addition of acid in order to obtain alicyclic 4-keto carboxylic acid derivs. 2-(2-Nitrovinyl)furan (I) was prepared from furfural and MeNO2 with NaOH catalyst; I heated with 20 parts concentrated HCl gave 6-nitro-4-oxocaproic acid. An unknown compound (obtained by ring cleavage of difurfurylideneacetone), leaflets, m. 152-4°, showed a mol. weight of 272. Similarly, the ring cleavage reactions were tried for 2-furanacrylonitrile, m. 127°, prepared from furfural and MeCN; 1,2-dihydroxy-1,2-difurylethane, needles, m. 130-1°, prepared by hydrogenation of furoin in EtOH at 65°, followed by vacuum distillation, and other derivs.

IT 7187-01-1P, 2-Furanacrylonitrile
RL: PREP (Preparation)
(preparation of)

RN 7187-01-1 CAPLUS
CN 2-Propenenitrile, 3-(2-furanyl)- (CA INDEX NAME)



L5 ANSWER 126 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1955:15976 CAPLUS
DOCUMENT NUMBER: 49:15976
ORIGINAL REFERENCE NO.: 49:3137a-i,3138a-i,3139a-i,3140a-i,3141a-i,3142a-i,3143a-i,3144a-i,3145a-i,3146a-i,3147a-i,3148a-i,3149a-i,3150a-i,3151a-b
TITLE: Oxazoles and oxazolones
AUTHOR(S): Cornforth, J. W.; Clarke, H. T.; et al.
CORPORATE SOURCE: Oxford Univ.; Princeton Univ. Press
SOURCE: Chemistry of Penicillin (1949) 688-848
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB OXAZOLE SECTION: New methods for constructing the oxazole ring have been devised and the behavior of functional groups elucidated. The synthesis of oxazoles and imidazoles from K β-hydroxy-α-(α-alkoxyalkylideneamino)acrylates is given. A mixture of 51.1 g. AmCN and 24.5 g. EtOH was kept with 19.2 g. dry HCl below 0° for 2 wk, decomposed with 74 g. K2 CO3 in Et2O and distilled The crude AmC(OEt):NH (62.4 g.), b11 52-65°, was shaken with cold aqueous H2NCH2CO2Et.HCl for 1 h. The upper layer was fractionated to yield Et α-ethoxycaprylideneaminoacetate (I), b0.5 91°, saponified on gentle warming to AmCO2Et. The corresponding Me α-methoxycaprylideneaminoacetate (Ia), b0.1 74°, was similarly prepared A solution of 0.85 g. K in 2.5 g. EtOH and 14 g. Et2O was diluted to 50 mL. with Et2O, cooled to -15° and treated with a similarly cooled mixture of 4.85 g. I and 3.2 g. HCO2Et, yielding after 3 h. at -10°, 2.6 g. of hygroscopic needles of C5H11C(OEt):NC(CO2Et):CHOK (II). The corresponding K Me β-hydroxy-α(α-methoxycaprylideneamino) acrylate (IIa) was obtained in 3.2 g.-yield from 3.75 g. Ia. Treatment of 2.6 g. II and 1.25 g. DL-penicillamine in 5 cc. EtOH with alc.-HCl gave crystalline DL-N-caproylpenicillamine, m. 137-8°. Treatment of II with ethereal HCl produced Et 2-amyl-oxazole-4-carboxylate, b0.07 99° (dinitrophenyl-hydrazone, m. 165-6°; amide, m. 152°) saponified to 2-amyl-oxazole-4-carboxylic acid, m. 92-3° (PhNH2 salt. m.98.5-9.5°) readily decarboxylated to 2-amyl-oxazole, b. 172-3°; picrate, m. 84.5-5.5°. This general synthesis of 2-substituted oxazoles and their 4-carboxylic acids has been extended to Et 2-phenyloxazole-4-carboxylate, m. 69-70°, the corresponding acid, m. 209°, and carried through to the known 2-phenyloxazole. The method can be also applied to the synthesis of imidazoles. Treatment of I with aqueous NH4OH gave 2-amylimidazole-4-carboxylic acid, m. 230° (decomposition); with MeNH2.HCl or alc. H2NCH2CO2Et.HCl, I produced, resp., Et 2-amyl-1-methylimidazole-4-carboxylate (III), m. 42-3°, and Et 2-amylimidazole-4-carboxylate-1-acetate (IIIa), m. 61°. Similarly, Ia gave Me 2-amyl-1-methylimidazole, m. 66.7°, and Me 2-amylimidazole-4-carboxylate-1-acetate, m. 107°. Hydrolysis of III and IIIa yielded 1-methyl-2-amylimidazole-4-carboxylic acid, m. 121-3°, and 2-amyl-4-carboxyimidazole-1-acetic acid, m. 132-4°. Starting from PhCH2CN, Et 2-benzylimidazole-4-carboxylate-1-acetate, m. 111-2°, was likewise prepared, converted by treating with MeOH into a Me Et ester. On heating with aqueous NH4OH and with PhNH2, 2-amyl-oxazole-4-carboxylic acid was converted into 2-amylimidazole, m. 33-4° and 1-phenyl-2-amylimidazole, m. 143-4°. Synthesis of oxazoles by rearrangement of oxazolones. The Na salt of 2-benzyl-4-hydroxymethylene-5-oxazolone (2.7 g.) in 50 mL. absolute MeOH was treated with 5 mL. absolute Et2O containing 0.38 g. HCl. The gummy product (2.28 g.) was taken up in 10 mL. absolute MeOH and heated for 30 min. with 6.2 mL.

L5 ANSWER 126 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
H2O contg. 0.42 g. NaOH. The residue on evapn. was dissolved in 10 mL. of iced H2O, acidified with dil. HCl to pH 6.5 and extd. with Et2O, yielding 700 mg. 2-benzyloxazole-4-carboxylic acid, m. 158°. On heating at 220°, crude 2-phenyl-4-(α-hydroxyethylidene)-5-oxazolone rearranged to 2-phenyl-5-methyloxazole (IV), m. 184-5° (decompn.). Similarly, on heating to 230°, Na 4-hydroxymethylene-g-amyl-5-oxazolone rearranged to 2-amyl-oxazole-4-carboxylic acid. Evapn. of 2-(1-pentenyl)-4-(hydroxymethylene)-5-oxazolone in NaOH and fusion of the residue at 250° under reduced pressure yielded 2-pentenyl-oxazole-4-carboxylic acid, m. 145-7°. Incidental syntheses of oxazole derivs. The action of PhSO3Ag on Me thiobenzylpenaldate di-Et acetal produced colorless prisms of 2-benzyloxazole-4-carboxylic acid, m. 156-7° and the dehydration of Et α-benzylamino-acetoacetate gave Et 2-phenyl-5-methyloxazole-4-carboxylate, m. 51-2°, hydrolyzed to the acid, m. 180-1°, decarboxylated at 220° in the presence of a trace of CuO to IV. Thus a reaction known to succeed with α-acylamino ketones and carboxylic esters is extended to β-keto esters. The 2-substituted oxazoles and their 4-carboxylic acids and esters are feebly basic, readily oxidized by cold aq. KMnO4 but stable to Br in CCl4. The ring opens on warming with 2,4-(O2N)2C6H3NHNH2 in 2N HCl with a tendency to formation of glyoxal osazone derivs. Rosenmund redn. of 2-amyl-oxazole-4-carboxylic acid chloride produced 2-amyl-oxazole-4-carboxaldehyde, b8 108° (2,4-dinitrophenylhydrazone, m. 172-3°), converted by warming with D-penicillamine-HCl in AcOH to the thiazolidine, devoid of antibiotic properties. From the corresponding Et ester, 2-benzyl-4-carboxyoxazole hydrazide, m. 81-3° and benzylamide, m. 121-2° were prepd. In attempts to synthesize the thiazolidine-oxazolone structure for penicillin, attention was directed to the prepn. of 5-alkoxyoxazoles and many variations of the general method of dehydrating α-acylamino esters with P2O5 were introduced. By the use of PCl5, P2O5, POCl3, SOCl2, and PhSO2Cl, the following new oxazoles were prepd. (substituent given): 2-Ph, 5-MeO, b9 141°; 2-Ph, 5-PhCH2O, m. 56°; 2-PhCH2, 5-EtO, b15 152-4°; 2-PhCH2, 5-MeO, m.31-2°; 2-Am, 5-EtO, b0.8 82-5°; 2-Am, 5-MeO, b1.0 60-65°; 2-(1-C5H9), 5-EtO, b20 125-8° (C5H9 = pentenyl); 2-(1-C5H9), 5-MeO, b15 108-10°; 2-PhCH:CH, 5-EtO, m. 35°; 2-PhCH:CH, 5-Ph CH2O, picrate, m. 135° (decompn.); 2-Ph, 4-Me, 5-EtO, b10 151°; 2-Ph, 4-Me, 5-PhCH2O, picrate, m. 112-13°; 2-PhCH2, 4-Me, 5-EtO, b15 145-50°; 2-Am, 4-Me, 5-EtO, b3 92°; 2,4-Ph2, 5-EtO, m. 47-8°; 2-Ph, 4-PhCH2, 5-EtO, picrate, m. 105°; 2-Ph, 4-PhCH2, 5-PhCH2O, picrate, m. 117°; 2,4-(PhCH2)2, 5-EtO, b0.3 145-50°; 2-Am, 4-PhCH:CH, 5-EtO, m. 92°; 2-Ph, 4-CO2Et, 5-EtO, m. 75°; 2-Am, 4-CO2Et, 5-EtO, b0.1 122-5°; 2-(1-C5H9), 4-CO2Et, 5-EtO, b0.2 125°; 2-PhCH2, 4-CO2Et, 5-EtO, b0.1 165°. The possibility of converting an alkoxyoxazole to the corresponding oxazolone was realized by the catalytic hydrogenation of 2 g. of 2-phenyl-5-benzyloxyoxazole in 30 mL. dry dioxane in the presence of Pd-black to 2-phenyl-5-oxazolone, m. 91°. The converse reaction, transformation of an oxazolone to an alkoxyoxazole, has also been achieved. Methylation of 3 g. of 2-phenyl-4-carbethoxy-5-oxazolone with 500 mg. CHZN2 in 50 mL. Et2O yielded 2-phenyl-4-carbethoxy-5-methoxyoxazole, m. 72°. Similarly, methylation of 2-phenyl-4-carbomethoxy-2-oxazolin-5-one gave 2-phenyl-4-carbomethoxy-5-methoxyoxazole, m. 98°, identical with that prepd. by the dehydration of BzNHCH(CO2Me)2 with PCl5 in CCl4. Attempts to obtain 5-alkoxyoxazole-4-carboxaldehydes covered a wide range. Formylation of BzNHCH2CO2Et and condensation with PhCHZNH2 in Et2O gave Et β-benzylamino-α-benzamidoacrylate, R'NHCH:C(CO2Et)NHCOR (V; R = Ph, R' = PhCH2), m. 108°, cyclized by PBr3, POCl3 or PCl5 to 2-phenyl-4-benzylaminomethylene-5-oxazolone (VI), m. 134-7; Ac deriv., m. 140°. In the same way, Et β-benzylamino-α-phenylacetamido acrylate (VIa) with PBr3 gave 2-benzyl-4-benzylaminomethylene-5-oxazolone (VIb). Dehydration of Et α-benzamido-β,β-diethoxypropionate with PCl5-POCl3 yielded 2-phenyl-4-(ethoxymethylene)5-oxazolone (VII). Distn. of benzyl α-benzamido-β,β-diethoxypropionate gave a mixt. of products including benzyl α-benzamido-β-ethoxyacrylate, m. 108-10°; benzyl 2-phenyloxazole-4-carboxylate, m. 106-7°; and VII. Attempts were made to cyclize α-benzyl-β-methyl-DL-phenylpenicilloate, HN.CH(CO2R').CMe2.S.CHCH(NHCOR)CO2CH2Ph (VIII, R = Ph, R' = Me) (VIIIa), m. 130°; dibenzyl-DL-phenylpenicilloate (VIII, R = Ph, R' = PhCH2) (VIIIb), m. 107-8°; and DL-2-(carboxy-1-hexenoylaminomethyl)-5,5-dimethyl-4-carbometh-oxythiazolidine benzyl ester (VIII, R = 1-pentenyl, R' = Me). (VIIIc). The action of PCl5 on VIII and VIIIa gave definite evidence of formation of thiazolidinylalkoxyoxazoles and cyclization of VIIIb and chromatog. purifn. of the product gave benzyl 2-(2-phenyl-5-benzyloxy-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylate, m. 120-5°, absorption band at 2850 A. This reduced in EtOAc using a Pd-BaSO4 catalyst with 2 mol H, corresponding to removal of 2 PhCH2 groups, yielded a product with no-antibiotic activity. The simpler thiazolidines were also investigated. The reaction of 3-methyl-2-(benzamidocarbethoxymethyl)-thiazolidine with PCl5 gave a Cl-contg. product, converted by NaHCO3 to a probable sulfoxide. With PCl3, a product was obtained, which was converted by aq. KOH to 2-phenyl-4-hydroxymethylene-5-oxazolone. β-Methylaminoethyl mercaptan-HI (from 15 g. of-2-methylthiazoline-MeI) in 20 mL. H2O was treated with 11 g. of crude Na salt of C,N-diformylglycine Et ester and neutralized with AcOH. After 15 h., NaHCO3 was added and the dried CHCl3 exts. (120 mL.) were concd. to give 6.55 g. of crude product, converted by treatment with 65.5 mL. of 10% HCl in EtOH to 4.4 g. of 2-(aminocarbethoxymethyl)-3-methylthiazolidine-2HCl (IX), m. 169-70° (decompn.). IX (10.0 g.) in 36.1 mL. of 2N NaOH and 35 mL. EtOH was stirred with 6.6 g. PhCH2CS2Me for 45 h., yielding 6.2 g. of colorless prisms of 2-[(phenylthioacetamido)carbethoxymethyl]-3-methylthiazolidine (X), m. 100-100.5°. Addn. of 5.0 g X in 20 mL. CHCl3 to 8.6 g. PhSO3Ag and 2.5 mL. pyridine in 70-mL. CHCl3 gave no identifiable org. products. The action of PhSO3Ag on Me α-phenylthioacetamido-β,β-diethoxypropionate yielded a product from which Me-benzylpenaldate and 2-benzyloxazole-4-carboxylic acid were isolated. By the PCl5 method it has been possible to prep. 4-(2-thiazolyl)-2-benzyl-5-ethoxyoxazole and 2-(p-nitrophenyl)-4-(5,5-dimethyl-4-carbomethoxy-2-thiazolinyl)-5-ethoxyoxazole. Attempts to introduce a CHO group into the 4-position of 2-phenyl-5-ethoxyoxazole (XI) using PhNMeCHO and POCl3 gave 2-phenyl-4-anilinomethylene-5-oxazoline. With AcNHBr, XI gave 2-phenyl-4-bromo-5-ethoxyoxazole, b0.8 128°. The oxidn. of 2-phenyl-4-methyl-5-ethoxyoxazole with SeO2, CrO3 or Cr2O2Cl2 resulted only in far-reaching breakdown. Condensation of PhCH2CH2COCO2H with AcNH2 or AmCONH2 gave α-acetamido- and α-caproyl-amino-γ-phenylisocrotonic acid (XII). Treatment of the Et ester of XII with PCl5 afforded 2-amyl-4-styryl-5-ethoxyoxazole (XIII), disrupted by ozonization with prodn. of BzOH and H2NCOCO2Et. XIII (5.7 g.) in 100 mL. glacial AcOH was stirred with 9.0 g. of Pb(OAc)4 for 3 h., yielding 6.1 g. of 2-(1-acetoxyamyl)-4-styryl-5-ethoxyoxazole, m. 90-1°, degraded by distn. with loss of AcOH to 2-(1-pentenyl)-4-styryl-5-ethoxyoxazole (XIV), m. 100°, reduced catalytically to XIII. Oxidn. of 2.83 g. XIV in 30 mL. tert-BuOH contg. 0.75 g. H2O2 and 30 mg. OsO4 at 40-50° for 2 h. produced PrCHO and 5-ethoxy-4-styryl-oxazole-2-carboxaldehyde, m.130.5°, converted into the thiazolidine, m.

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L5 ANSWER 126 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
169°, using DL-penicillamine. Cyclization of AmCONHCH(CO2Et)2 in dry alc. free CHCl3 with PCl5, yielded 2-amyl-5-ethoxyoxazole-4-carboxylic acid (XIV), m. 63.4°, which on refluxing with PCl5 in CHCl3 gave Et 2-amyl-5-chlorooxazole-4-carboxylate (XV), b0.3 106°, catalytically reduced over Pd-BaSO4 in xylene to 2-amyl-oxazole-4-carboxylate, acidified to the free acid (XVa), m. 93-4°, converted by alc. EtONa to XIV. Treatment of 2 g. XVa with 1.09 g. PCl5 in 10 mL. CHCl3 and distn. produced the corresponding acid chloride, b0.3 96°, converted by (NH4)2CO3 in aq. NH4OH to the amide, m. 90°, which, distd. with P2O5, gave 2-amyl-5-chloro-4-cyanooxazole (XVb), b0.15 72°. Redn. of 3.0 g. XVb in a suspension of 5.7 g. anhyd. SnCl2 in 40 mL. dry ether yielded unstable 2-amyl-5-chloro-oxazole-4-carboxaldehyde (XVI) (dinitrophenylhydrazone, m. 109-10°), rearranging in 3 days at room temp. or on low pressure distn. to 2-amyl-oxazole-4-carboxylic acid chloride. Despite its instability, XVI readily combined with D-penicillamine-HCl to produce D-2-(2-amyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carbo-xylic acid-HCl, m. 150-2° (decompn.). A similar series of compds. starting with Et 2-phenyl-5-ethoxyoxazole-4-carboxylate (XVII) and proceeding to the thiazolidine was later prepd. XVII was sapond. to the cryst. acid (XVIIa), m. 148°, converted to the acid chloride (XVIIb), m. 105-6°, and to Et 2-phenyl-5-chlorooxazole-4-carboxylate, m. 68°, by refluxing in xylene for 1 h. The corresponding acid (XVIII), m. 178-4° (decompn.), was converted through the acid chloride, m. 118-20°, the amide, m. 183°, and the cyano compd., m. 112°, to 2-phenyl-5-chlorooxazole-4-carboxaldehyde (XIX), m. 91-3°. The addn. of 1.14 g. aldehyde in 5 mL. EtOH and 10 mL. Et2O to 0.93 g. D-penicillamine-HCl in 5 mL. H2O and 0.65 g. AcONa, and passage of HCl through a filtered ethereal soln. of the reaction product, yielded 1.5 g. of 2-(2-phenyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylic acid-HCl, m. 178° (decompn.); Me ester-HCl, m. 120-2°; free acid, m. 166°; Me ester, m. 154°; PhCH2 ester, m. 116-7°. The thiazolidine exhibited a low order of antibiotic activity. A similar series of 2-benzyloxazole derivs. have been prepd. but the corresponding thiazolidine was inactive: 2-benzyl-5-ethoxy-oxazole-4-carboxylic acid, m. 118° (decompn.); Et ester, b0.1 165°; acid chloride, m. 81-2°; 2-benzyl-5-chlorooxazole-4-carboxylic acid, m. 183° (decompn.); Et ester, b0.02 170-5°; acid chloride, m. 156-7°; cyano compd., m. 49-50°; aldehyde [dinitrophenylhydrazone, m. 173°; semicarbazone, m. 185° (decompn.)]; 2-(2-benzyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carbo-xylic acid-HCl, m. 176-7° (decompn.). By refluxing 223 mg. XVIII in 3 mL. EtOH with 40 mg. Na, the Cl was replaced by the EtO group with formation of the corresponding acid, XVIIa. Distn. of the aldehyde XIX at 0.1 mm. gave 2-phenyloxazole-4-carboxylic acid chloride, m. 107-8°, transformed by stirring with cold concd. aq. NH4OH to the amide. Similarly the acid chloride XVIIb was converted to the amide, m. 118-19°, rearranged by heating for a few min. at 140° to Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 183deg;. All oxazoles found to undergo rearrangement may be formulated as 5-substituted oxazoles having a CO group in the 4-position, the general case being N:CR'.O.CR3:CCOR2 → N:CR'.O.CR2:CCOR3. Known examples of rearrangement are tabulated. Since the mol. is unstable when R3 and R2 are Et and Cl, resp., or when R3 and R2 are Cl and H, resp., it is deduced that the ethoxy aldehydes should show too great stability for successful synthesis. Cyclization of AmCONHCHCNCO2Et with P2O5 in CHCl3 gave 2-amyl-4-cyano-5-ethoxyoxazole, b0.03 98°, not reduced to the aldehyde by SnCl2 in Et2O. No 4-acetyloxazole was obtained from the MeHgI

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reaction product but the isolation of Et α-caproylaminoacetoacetate (dinitrophenylhydrazone, m. 166-7°) indicated oxazole ring cleavage. The dehydration of 2-phenyl-5-ethoxyoxazole-4-carboxyamide with POCl3 or the ethylation with MeCHN2 of the crude oxazolone obtained by treating BzNHCHCNCO2H with Ac2O produced 2-phenyl-4-cyano-5-ethoxyoxazole, m. 77°. The previously unknown 5-aminooxazoles were prepd. thus: treatment of 7 g. BzNHCH(CN)CO2Et, m. 138°, in 125 mL. CHCl3 with 6.2 g. PCl5 gave 4.5 g. Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 185°, also prepd. by the action of POCl3 on Bz-NHCH(CONH2)CO2Et. Condensation of 1.18 g. H2NCH-(CO2Et)2 with 1.13 g. PhNHOEt by heating for 30 min. at 110° gave the alternative compd., formulated as 2-phenyl-4-carbethoxy-5-imidazolone, m. 275°. Similarly were prepd. Et 2-benzyl-5-aminooxazole-4-carboxylate (XX), m. 124° and the corresponding 2-benzyl-4-carbethoxy-5-imidazolone, m. 254° (decompn.); 2-(1-pentenyl)-4-carbethoxy-5-aminooxazole, m. 105°; 2-amyl-4-carbethoxy-5-aminooxazole (XXa), m. 104° and the corresponding 2-amyl-4-carbethoxy-5-imidazolone., m. 230° (decompn.). On heating at 170° for 5 min., XXa was entirely converted into AmCONHCH(CN.)CO2Et, m. 83°. Heating either XX or PhCH2CONHCH(CN)CO2Et at 160-70° for 15 min. produced an equil. mixt. with the open chain ester predominating. This same mixt. was formed by heating 2-benzyl-5-ethoxyoxazole-5-carboxylic amide, probably through initial rearrangement to the aminooxazole. Stirring 35 g. NCCH2CO2CH2Ph in 40 mL. of chilled glacial AcOH with satd. aq. NaNO2 (16.5 g.) yielded 29 g. NCC(NOH)CO2CH2Ph, m. 119°, reduced with Al-Hg to NCC(NH2)CO2CH2Ph, m. 95°, and benzoylated to NCCH(NHBz)CO2CH2Ph, m. 130°, converted by heating at 160° for 5 min. to 2-phenyl-4-carbobenzyloxy-5-aminooxazole, m. 203°. The 4-carbethoxy-5-aminooxazoles are feebly basic substances whose HCl salts dissoc. readily. XXa.HCl, on boiling with ethereal EtOH gave AmCONHCH(CONH2)CO2Et, m. 150-1°, along with NH4Cl. Treatment of 1 g. XXa in 10 mL. dry Et2O at -15° with NOCl gave a low yield of Et 2-amyl-oxazole-4-carboxylate, m. 92-3°. Formylation of 15 g. BzNHCH2CN in 200 mL. HCO2Et and 100 mL. benzene by addn. of NaOEt (from 2.16 g. Na) in 100 mL. benzene produced, after treatment of the intermediate BzNHC(:CHONa)CO2H with dil. H2SO4 to pH 4, 2-phenyl-5-aminooxazole-4-carboxaldehyde (XXI), m. 172-3°, probably in the tautomeric form. Formylation of AmCONHCH2CN and distn. of the product yielded 2-amyl-oxazole-4-carboxylic acid amide, m. 154-5°, evidently by rearrangement of XXI. The action of POCl3 on Bz-NHCH(CONH2)2 and AmCONHCH(CONH2)2, m. 231°, gave 2-phenyl-5-amino-4-cyanooxazole, m. 233° (Ac deriv., m. 202-3°), and 2-amyl-5-amino-4-cyanooxazole, m. 117°. These aminooxazoles could not be reduced to aldehydes.

Satn. of 0.52 g. PhCH2CSNHCH(CN)CO2Et, m. 157°, treated in 5 mL. dry EtOH with dry HCl at -10° and the soln. evapd. after 12 h. at 20° in vacuo yielded 0.5 g. 2-benzyl-4-carbethoxy-5-aminothiazole, m. 180°. OXAZOLONE SECTION. Part. I. General Chem. of Oxazolones. Prepn. of 2-Oxazolin-5-ones. The reaction of Ac2O with α-acylamino acids is the most general procedure by which new oxazolones, O.CR:N.CR1R2.CO, have been prepd. (substituents given): 2-Me, 4-iso-Pr, b10 60°; 2-PhCH2, 4-Me, b0.5-1.0 122-3°; 2-PhCH2, 4-iso-Pr, b0.5 115-17°; 2,4-(PhCH2)2, oil; 2-Am, 4-PhCH2, b5 135-8°; 2-(2-pentenyl), 4-PhCH2, b1.0 155-7°; 2-PhCH2, 4,4-Me2 (I), m. 59.5°; 2-Ph, 4-iso-Bu, m. 56-7°; 2-PhCH2, 4-sec-Bu, b2.0 137-9°; 2-Ph, 4,4-C5H10, m. 71°; 2-PhCH2, 4-Me, 4-PhCH:CH, m. 56-7°; 2-Ph, 4-CO2Et, m. 147-8°; 2-Am, 4-CO2Et, oil; 2-Ph, 4-(p-MeOC6H4CH2); 2-PhCH2, 4-(p-MeOC6H4CH2); and 2-PhCH2, 4-iso-Bu. Similarly, heating 100 g. BzNHCH2CO2H (II) in 300 mL.

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Ac2O at 100° yielded 49 g. 2-phenyl-2-oxazolin-5-one (III), m. 94-5°, the only monosubstituted oxazolone prepd. by this method. By warming BzNHCHPhCH2CO2H in CHCl3 with 1 equiv. of 2-benzyl-4-methyl-5-oxazolone, a good yield of 2-phenyl-4-benzyl-5-oxazolone, m. 68-9°, was obtained. Addn. of 1 g. NaNO2 in 20 mL. H2O to 3 g. of BzNHC(CONHNH2):-CHPh in 30 mL. N HCl gave α-benzamidocinnamic azide, m. 113-4° (decompn.), converted on boiling with EtOH or treatment with pyridine at room temp. to 2-phenyl-4-benzylidene-5-oxazolone (IV). Similarly, Me2C:C(NHBz)-CON3 was converted to 2-phenyl-4-isopropylidene-5-oxazolone (IVa). These type II (unsatd. substituent at the 4-position) unsatd. oxazolines are formed more readily than the above-listed type I (satd. substituent at the 4-position) satd. oxazolones to which the azide conversion could not be extended. Redn. of IV over Pd-C gave 2-phenyl-4-benzyl-5-oxazolone (V), m. 67-8°. IVa was similarly reduced in dioxane to give an oil which, treated with PhNH2 in benzene, produced Me2CHCH(NHBz)CONHPh, m. 211-2°. The possibility arose that any reagent capable of transforming an acid to its chloride might be expected to convert an α-acylamino acid to the corresponding oxazolone. Thus treatment of II in 15 mL. dioxane with 2 mL. PBr3 gave III. Similarly, 14.5 g. PhCH2CONHCMe2CO2H in 150 mL. dioxane was treated with 18 g. PBr3. The solid product suspended in dioxane and treated with slight excess of CH2N2 in ether yielded I, converted by PhCH2NH2 into PhCH2CONHCMe2CONH2, m. 122-3°. Treatment of PhCH2CHNHBzCO2H in pyridine with PBr3 likewise gave the known V. Attempts to prep. 2-benzyl-5-oxazolone from PhCH2CONHCH2CO2H gave an unstable oil, converted by PhCH2NH2 into PhCH2CONHCH2CONHCH2Ph. Conversion of PhCH:C(NHBz)CO2H into IV was effected by POCl3, SOCl2, pyridine, by ClCH2COCl and K2CO3, and by AcCl in dioxane. Oxazolones have been produced by treating PhCH2OCOCl with acylamino acids. Apart from direct dehydration, three methods are known for the prepn. of type II oxazolones; the Erlenmeyer aldehydeacylglycine synthesis, the Bergmann-Stein reaction of N-(α-haloacyl)amino acids with Ac2O, and the dehydration of β-hydroxy-α-acylamino acids. In that III reacts with Me2CO in the presence of NaOAc to yield IVa in the absence of Ac2O, it is suggested that III is an intermediate in the Erlenmeyer synthesis. In the presence of a little pyridine, BzH condenses with III to produce IV. Similarly, 2-phenyl-4-propylidene-5-oxazolone, m. 88-9°, was obtained in good yield from III and EtCHO. By adding Ac2O dropwise with stirring to 17.9 g. II and 6.1 g. fused NaOAc in 580 mL. Me2CO, refluxing for 3-4 h. at 59-62°, pouring the reaction mixt. over 200 g. ice and dilg. to 1500 mL. produced high yields (73%) of relatively pure 2-phenyl-4-isopropylidene-5-oxazolone, m. 98°. Condensation of II with (EtO)2CHCHO and Ac2O gave 4,4'-glyoxalidenebis(2-phenyl-5-oxazolone), m. 325° (decompn.). Though no acyl interchange in the Erlenmeyer synthesis occurs with II, the formation of 2-methyl-4-benzylidene-5-oxazolone occurs when either PhCH2CONHCH2CO2H or AmCONHCH2CO2H (VI) is refluxed with BzH in the presence of Ac2O and NaOAc. Refluxing VI (15.1 g.) with 13.1 g. AmCO2Na and 61 g. (AmCO)2O in 49 mL. Me2CO for 24 h. at 75° gave α-caproyl-amino-β,β-dimethylacrylic acid, m. 162-3°, converted by melting and heating in vacuo at 180-90° into 2-amyl-4-isopropylidene-5-oxazolone, b0.03 60-2°. By Bergmann's method, 2-methyl-4-isopropylidene-5-oxazolone (VII) and 2-methyl-4-sec-butylidene-5-oxazolone were prepd. from Me2CHCH2CH(NHCOCH2Cl)CO2H and EtMeCHCH-(NHCOCH2Cl)CO2H. Carter's method was used to prep. VII by the action of Ac2O on Me2C(OMe)CHNH2CO2H. Ring opening Reactions of Oxazolones. The general reaction of oxazolones with H2O, ROH, RSH, NH3, RNH2 and RR'NH represented by O.CR:N.CR1R2.CO + HX → OCRHNCR1R2COX, suggested originally the thiazolidine-oxazolone formulation of penicillin.

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Comparison of the reactivity of V with that of IV showed the former to be rapidly hydrolyzed by 2N aq. acid or alkali under conditions not affecting the latter. V reacts with ROH more rapidly than III. In the presence of NaOMe or PhCH2NMe3-OH, IVa was converted quant. to Me2C:C(BzNH)CO2Me, m. 130-1°. The methanolysis of 2-benzyl-4-p-methoxybenzyl-5-oxazolone in dry abs. MeOH yielded (N-phenylacetyl-p-methoxyphenylalanyl)-p-methoxyphenylalanine, m. 199-200°. The formation of the dipeptide may be due to an "ortho-ester" reaction with the imino-ether form of the oxazolone. Reaction of PhCH2SH with III and I yielded benzyl hippurate, m. 101-2° and Me2CHCH(NHCOCH2Ph)COSCH2Ph, m. 138.5°. Almost all types of oxazolones react with PhCH2NH2 to form α-acylaminoacyl-benzylamides. The reaction of V with d-MePhCHNH2 in dry dioxane was followed polarimetrically and at const. rotation, produced N-benzoylphenylalanine-d-N-α-phenylethylamide, m. 178-80°, [α]D23 28.5° (c 1, dioxane). The strongly enolyzed 2-phenyl-4-carbethoxy-5-oxazolone formed a salt with PhCH2NH2, converted on heating in xylene to the benzylamide, m. 132°. The reaction of PhNH2.HCl with III and 2-benzyl-4-sec-butyl-5-oxazolone gave the normal anilide and the corresponding acid. Reaction of V and 2-phenyl-4-isobutyl-5-oxazolone with L-HSCH2CH-(NH2)CO2Me produced the normal amides, m. 128-9°, and 131-5°, resp., the NH2 group taking precedence over the SH group in the condensation. The action of N2H4 on oxazolones has been clarified. The addn. of 18 g.-phenyl-4-methyl-5-oxazolone to excess 60% N2H4.H2O in EtOH and heating to 50-60° for 30 min. gave 17.5 g. benzoylalanine hydrazide, m. 142-4°; benzylidene deriv., m. 193-4°. Treatment of IV with N2H4.H2O also gave the normal hydrazide, PhCH:C(NHBz)CONHNH2, m. 113-14°, converted by heating the corresponding azide in xylene to 2-oxo-4-benzylidene-6-phenyl-1,3,5-oxadiazine, m. 174° (decompn.). Conversion of Me2C:C(NHBz)CON3 similarly produced 2-oxo-4-isopropylidene-6-phenyl-1,3,5-oxadiazine, m. 166-8°. A mixt. of 5 g. IV, 10 mL. N2H4.H2O and 3 mL. EtOH was refluxed for 30 min. yielding 4-benzamido-3-phenyl-5-pyrazolidone, m. 228-9°, identical with the product formed by refluxing PhCH:C(NHBz)CONHNH2 (VIII), m. 157-8°, which N2H4.H2O for 30 min. Similarly, the hydrazide Me2C:C(NHBz)CONHNH2, m. 192-4°, was converted into 3,3-dimethyl-4-benzoylamino-5-pyrazolidine, m. 106-8°. The hydrazide VIII was boiled in N NaOH and the sparingly sol. salt on acidification gave 6-hydroxy-5-benzyl-3-phenyl-1,2,4-triazine, m. 175-6°; Ac deriv., 187-8°. Oxidn. of XIII with K3Fe(CN)6 produced N,N'-bis(α-benzoylaminocinnamoyl)hydrazine, m. 265°, together with a substance, m. 186-7°, with the probable structure PhCH:C.CH(OH).NBz.C-(:CHPh).CH(OH).NBz, forming PhCH2CH(NHBz)-(CO2H) on alk. hydrolysis. REACTIONS OF TYPE II OXAZOLONES: Some reactions involving the double bond in type II oxazolones have been discovered. Treatment of IV in dry dioxane with 2 mol CH2N2 in dry Et2O at 0° and allowing the soln. to stand overnight at room temp. gave product, C17H13O2N, m. 142-3°. Addn. of liq. NH3 to IVa with shaking and cooling in solid CO2 gave a small yield of basic product, C12H17O2N3, m. 162-6°, probably by addn. of 2 mol NH3. Addn. of H2S and RSH to the double bond has been studied in connection with various syntheses of penicillamine. The addn., of 136 g. IVa in 675 mL. dry benzene to 3.38 g. Na in 675 mL. of chilled dry MeOH and 76.5 mL. PhCH2SH produced Me2CC(NHBz)CO2Me, m. 137-8°, and Me2C(SCH2Ph)CH(NHBz)CO2Me, m. 66-7°. The addn. probably takes place after ring opening, since the oxazolone can be replaced by an acrylic ester. Similarly, IV under like conditions, gave PhCH(SCH2Ph)CH-(NHBz)CO2Me, m. 164°. There is no evidence of direct addn. of PhCH2SH to the double bond. Addn. of H2S to IVa and VII in the presence of Et3N yielded Me2C(SH)CH(NHBz)COSH and Me2C(SH)CH(NHAc)COSH, resp. The initial step is probably the addn. of

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H2S to the double bond. Anhyd. MeOH satd. with H2S at 0° treated with IVa gave 2,5,5-trimethyl-2-thiazoline-4-carboxylic acid, b25 120°; picrate, m. 159°, probably formed by addn., followed by displacement. IV similarly yielded 2-phenyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m. 124-6°. IVa was apparently converted by treatment with alc. NaSH to 2-phenyl-4-isopropylidene-5-thiazolone, m. 100.5-101.5°. The reactivity of the Me groups in IVa is sufficient to permit condensation reactions with BzH to produce 2-phenyl-4-benzylideneisopropylidene-5-oxazolone, m. 135°. A mixt. of stereoisomers, m. 134-6°, was produced by heating a mixt. of 35.8 g. BzNHCH2CO2H, 32 g. PhCH:CHAc, 15 g. of fused NaOAc and 50 mL. Ac2O for 3 h. at 100°. IVa is a pseudo-acid and exhibits weak violet fluorescence in Et3N. On addn. of NaOMe to IVa in MeOH, the initial intense blue-violet fluorescence in UV light due to the presence of the propenyl-oxazole soon disappears with the formation of Me2C:C(NHBz)CO2Me by ring opening. Misc. REACTIONS OF OXAZOLONES. Excess PhMgBr was added to 6.0 g. 2-phenyl-4-methyl-5-oxazolone in Et2O and after refluxing for 6 h. the reaction product was hydrolyzed and extd. with Et2O, yielding 4.6 g. 1,1-diphenyl-2-benzoylamino-propanol, m. 192-3°. With AgClO4 in benzene, III in EtOH gave a complex, m. 146° (decompn.). A similar cryst. compd., m. 172°.(decompn.) was formed with 2-benzyl-4-methyl-5-oxazolone (IX). Formylation of 2,4-diphenyl-5-oxazolone apparently produced a stabilized enolic form, PhC:N.CPh:COH.O, m. 110°. Oxidn. of 2-phenyl-4-isobutyl- and 2-phenyl-4-benzyl-5-oxazolones with Hg(OAc)2 gave the corresponding 4,4'-bisoxazolones, m. 138-42°, and 201-202.5°, resp. PSEUDO-OXAZOLONES. According to the method of Bergmann, 12 g. PhCHBrCONHCH2CO2H was added to 5 mL. dry pyridine and 100 mL. Ac2O and after 2.5 h. at 0° was poured over ice. The solid product was dried over NaOH and crystd. from warm MeOH by cooling to -50°, yielding 64% of 2-benzylidenepseudooxazolone (2-benzylidene-3-oxazolin-5-one), m. 92-4°, hydrolyzed by 0.5N HCl in acetone to PhCH2-CONH2, m. 153-7°. An attempt to prep. 2-benzyl-4-methylene-5-oxazolone by Bergmann's method from Ph-CHClCONHCHMeCO2H gave the potent skin irritant 2-benzylidene-4-methylpseudo-5-oxazolone (X), m. 105-115°, hydrolyzed by aq. acetone to PhCH2CONH2 and AcCO2H, suggesting that the pseudooxazolones are intermediates in the Bermann synthesis of type II oxazolones and that, in general, the latter are in dynamic equil. with the pseudooxazolones. In an attempt to use pseudooxazolones for the thiazolidine-oxazolone structure suggested for penicillin, Br was added to V and the product condensed with penicillamine (XI) in the presence of AcOK and AcOH. The low order of activity noted was probably due to BrCH2COCO2H which has an activity of 6 units per mg. against Gram-pos. organisms. X (1 g.) in 40 mL. pure AcOEt was hydrogenated at several atm. pressure in the presence of 2 g. active Raney Ni to IX, suggesting that the thiazolidine-oxazolone structure might be accessible by redn. of the corresponding pseudooxazolone. Ice-cold pyridine (20 mL.) in 65 mL. Me2CO was mixed with 1 g. (EtO)2CHCH(NHCOCHBrPh)CO2H and after 3 h., the mixt. was poured over crushed ice, extd. with CHCl3, washed with aq. NaHCO3, dried by passage through acid-washed Al2O3, and the filtrate was evapd., yielding 4.8 g. oily 2-benzylidene-4-(diethoxymethyl)pseudo-5-oxazolone, which failed to condense with XI. In another attempt, (EtO)2CHCH(NHCOCHClPh)CO2Me was condensed with XI to give α-Me α-chlorobenzylpenicilloate (XII). On treatment of crude XII (5.2 g.) with a mixt. of 10.8 g. pyridine and 35.2 mL. Ac2O with shaking and cooling, a dark brown gum was formed, which, crystd. from Et2O at -50°, gave a "dehydropenicillin" (XIII), C16H16O4N2S, m. 90-5° (decompn.). Addnl. information in printed abstr.

IT 859734-15-9P, Urea, (α-cyanocinnamyl)- 875837-16-4P
, Benzamide, N-(1-cyano-2-hydroxyvinyl)-, benzoate

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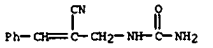
RL: PREP (Preparation)
(prepn. of)

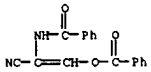
RN 859734-15-9 CAPLUS

CN Urea, (α-cyanocinnamyl)-·(5CI) (CA INDEX NAME)



RN 875837-16-4 CAPLUS

CN Benzamide, N-(1-cyano-2-hydroxyvinyl)-, benzoate (5CI) (CA INDEX NAME)



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AB cf. C.A. 42, 7732g. Addition of 26.5 g. CH2:CHCN over 1 h. at below 35° to 42 g. Me2C(OH)C.tplbond.CH and 3 g. 40% KOH, stirring 6 h. at room temperature, allowing the mixture to stand overnight, neutralization with 1:1 HCl, filtration, from KCl and distillation gave 57.5 g. Me2C(OCH2CH2CN)C.tplbond.CH (I), b18 96-6.5°, nD20 1.4356, d20 0.9275. Hydrogenation of this (25 g.) in MeOH saturated with NH3 over Raney Ni at 100-10° and 140 atmospheric H pressure gave 24.2 g. Me2EtCOCH2CH2CH2NH2 (II), b14 68-70°, nD20 1.4360, d20 0.8589. I (30 g.), 50 mL. H2O and 100 mL. dioxane treated with stirring with 3 g. HgSO4 and 2 drops H2SO4, then stirred 6 h. at 90° gave, after saturation with Na2CO3 and extraction with Et2O, 26.8 g. Me2CAcOCH2CH2CN, b18 132-6°, nD20 1.4357, d20 1.0033. Similar reaction of 54 g. Me2C(OH)CH:CH2 (III), 3.5 g. 40% KOH, and 35 g. CH2:CHCN gave 32.5 g. Me2C(OCH2CH2CN)CH:CH2 (IV), b16 94-6°, nD20 1.4337, d20 0.9056, and 33 g. initial ROH. Reaction of 42 g. III and 26.5 g. CH2:CHCN with 0.6 g. Na catalyst gave 43.2 g. IV and 8 g. initial ROH. Hydrogenation of the product in MeOH over Raney Ni gave 100% II, b7 56-8°. Reaction of 165 g. Me2C(OH)C.tplbond.CCH:CH2, 10 g. 40% KOH, and 53 g. CH2:CHCN gave 129.5 g. Me2C(OCH2CH2CN)C.tplbond.CCH:CH2, b6 93-4°, nD20 1.4710, d20 0.9334, which hydrogenated to Me2BuCOCH2CH2CH2NH2 (V), b18 102-4°, nD20 1.4485, d20 0.8630. Reaction of 88 g. Me2EtCOH, 2 g. powdered MeONa, and 53 g. CH2:CHCN (temperature rise to 40°, followed by stirring 4 h. at room temperature and standing overnight) gave 14 g. Me2EtCOCH2CH2CN (VI), b18 92-7°, nD20 1.4247, d20 0.8981, and 72.5 g. initial ROH; when 57 g. Me2EtCOH and 4 g. 40% KOH was treated with 35 g. CH2:CHCN no heat was evolved and the mixture was stirred 1 h. at 80°, cooled and neutralized, yielding 3.6 g. VI. Hydrogenation of this over Raney Ni gave 90% II, b7 56-8°. To 120 g. Me2BuCOH was added 1.5 g. K and 53 g. CH2:CHCN was added with cooling; after 2 h. the mixture was neutralized with HCl and treated as usual, yielding 24.3 g. Me2BuCOCH2CH2CN, b11 105-7°, nD20 1.4306, d20 0.8825; the same reaction run with 40% KOH catalyst gave a lower yield; hydrogenation over Raney Ni gave V, b6 78-81°, nD20 1.4482. To 101 g. (.tplbond.CCH2OH)2, 150 mL. dioxane, and 7 g. 40% KOH was added with cooling 125 g. CH2:CHCN below 35°; after 4 h. stirring at room temperature, 48 h. standing, and neutralization with HCl there was obtained 216 g. (.tplbond.CCH2OCH2CH2CN)2, b3 189-95°, nD20 1.4760, d20 1.0910, which hydrogenated as above in MeOH saturated with NH3 over Raney Ni yielding (CH2CH2OCH2CH2CH2NH2)2, b4 134-6°, nD20 1.4618, d20 0.9620. Addition of 50 g. CH2:CHCN to 59 g. (.tplbond.CCMe2OH)2, 200 mL. dioxane, and 4 g. 40% KOH gave no thermal effect; the mixture stirred 5 h. at 60-70° and 1 h. at 70-5°, allowed to stand 40 h., neutralized with HCl and worked up as usual yielded 37.6 g. HOMe2CC.tplbond.CCMe2OCH2CH2CN, b3 111-12°, nD20 1.4530, d20 0.9758, 32.1 g. (.tplbond.CCMe2OCH2CH2CN)2, b2.5 142-6°, nD20 1.4553, d20 0.9915, m. about 25° (after long standing), and 7.9 g. intermediate fraction. Hydrogenation as above over Raney Ni

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gave, resp., HOCH2CH2CH2CH2OCH2CH2CH2NH2, b4 91-4°, nD20 1.4587, d20 0.9321, and (CH2CH2OCH2CH2CH2NH2)2, b3.5 136-8°, nD20 1.4752, d20 0.9539.

IT 107-13-1, Acrylonitrile
(reaction with acetylenic alcs. and glycols)

RN 107-13-1 CAPLUS

CN 2-Propenenitrile (CA INDEX NAME)

L5 ANSWER 128 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1953:72719 CAPLUS
DOCUMENT NUMBER: 47:72719
ORIGINAL REFERENCE NO.: 47:12330g-i,12331a-i,12332a-c
TITLE: Azulenes. III. An attempted synthesis of 1-isopropyl-4,8-dimethylazulene. Migration of an isopropyl group
AUTHOR(S): Herz, Werner
CORPORATE SOURCE: Florida State Univ., Tallahassee
SOURCE: Journal of the American Chemical Society (1953), 75, 73-7
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. preceding abstract The usual diazoacetic ester method for the synthesis of azulenes, when applied to 1-isopropyl-4,7-dimethylindan (I), did not yield the expected 1-isopropyl-4,8-dimethylazulene (II), but vetivazulene (III). This is ascribed to a migration of the iso-Pr group from position 1 to position 2 of the azulene nucleus during or after the dehydrogenation with Pd-C catalyst. To 48 g. p-xylene, 96 g. AlCl3, and 720 cc. CS2 were added slowly with stirring and chilling 64 g. Me2CHCH:CHCOCl and, after 12 h., an addnl. 96 g. AlCl3 and 400 cc. CS2, the mixture was heated 3 h. on a steam bath, cooled, poured on ice-HCl, the organic layer separated, the CS2 removed in an air stream, the residual oil steam-distilled, the distillate extracted with Et2O, and the extract dried and fractionated to give 61 g. (66%) 3-isopropyl-4,7-dimethyl-1-indanone (IV), light yellow oil, b4 130-40°; 2,4-dinitrophenylhydrazone, m. 224° (from EtOAc). 2,5-Me2C6H3CH(CHMe2)CH2CO2H (V) (77 g.) heated on a steam bath 2 h. with 100 g. SOCl2 and let stand overnight yielded the chloride (VI) of V, b3 125-35°. To 55 g. AlCl3 in 200 cc. dry C6H6 was cautiously added 72.5 g. VI, and the mixture decomposed after 12 h. with ice-HCl and extracted with Et2O to yield 47.5 g. IV, b3 125-39°. IV (46.5 g.) reduced with Zn-Hg as previously described (loc. cit.) gave 32.5 g. (73%) I, b3 97-105°, b1.8 86-8°, nD25 1.5197. I (32 g.) treated with six 8-g. portions of N2CHCO2Et gave 19 g. recovered I, and 24 g. highly colored ester, b1 120-80°; this, refluxed 8 h. with 12 g. KOH, 25 cc. H2O, and 120 cc. EtOH, yielded 8.5 g. viscous, dark green acid, b2 165-85°, which was decarboxylated and dehydrogenated twice as previously described to yield 2.2 cc. crude trimethylazulene, b2 90-160°; the azulene in 25 cc. EtOH and 2 g. C6H3(NO2)3 (VII) in 75 cc. warm EtOH gave 0.42 g. azulene-VII complex which was chromatographed on Al2O3 with cyclohexane-C6H6 (3:1) as an eluant; the resulting violet-blue eluate was again converted to a VII-complex, violet needles, m. 151.5-2.5° (from EtOH); 7.5 mg. was passed through an Al2O3 column and eluted with spectral-grade isooctane to give a violet solution which showed an UV spectrum identical with that of III; the solution gave a 2,4,6-(O2N)3C6H2Me complex, m. 77.5-8° (from EtOH), and a picrate, black needles, m. 121-2° (from EtOH). In a 2nd run 71 g. I gave a total of 0.95 g. III, violet-blue liquid, b1 110-23°. When the azulene mixture was chromatographed, it was noticed that the first few drops of the cyclohexane eluate were blue; however, it was not possible to obtain sufficient material to permit characterization of the blue azulene, presumably II. 2,5-Me2C6H3COCHMe2 (VIII), 74.9 g. NCCH2CO2Et, 11.55 g. NH4OAc, 36 g. AcOH, and 150 cc. C6H6 refluxed 36 h. until the volume of H2O in the trap became constant gave 148 g. mixture of starting materials, and 51 g. (25%) 2,5-Me2C6H3C(CHMe2):C(CN)CO2Et (IX), b1 130-5°, m. 51° (from MeOH), nD25 1.5210. IX (10 g.) reduced 10 h. at room

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temp. over 5% Pd-C gave 6.5 g. (56%) 2,5-Me2C6H3CH(CHMe2)CH(CN)CO2Et (X), viscous oil, b2 130-8°, b1.2 122-4°, nD25 1.5038. X (5.5 g.) refluxed 18 h. with 55 g. 10% aq. KOH gave 2,5-Me2C6H3CH(CHMe2)CH(CO2H)2 (XI). XI decarboxylated by heating at 200° gave 2.1 g. V, m. 91.5° (from ligroine). In larger prepns., the theor. amt. of H was taken up only after repeated addn. of fresh catalyst and the hydrolysis proceeded very slowly to give from 136 g. IX, 46 g. (42%) V, b3 150-70°, and 23 g. acidic material, b3 170-90°, which was hydrogenated with PtO2 in EtOH to give an addnl. 15.5 g. V; amide of V, m. 119-20° (from ligroine). A Reformatskii reaction with 137 g. VIII and several portions of BrCH2CO2Et and Zn as previously described (loc. cit.) gave 89 g. recovered starting material and 15.5 g. distillate, b1.8 90-130°, which was refluxed with 8 cc. POCl3 in 125 cc. dry C6H6, and the resulting material (10.5 g.), b3.5 110-50°, hydrolyzed with 25 g. 50% alc. KOH to give 6.3 g. 2,5-Me2C6H3C(CHMe2):CHCO2H (XII), b2.5 130-45°, b4.5 150-2°. Catalytic hydrogenation of 5 g. XII over PtO2 and subsequent hydrolysis with 16 g. 40% KOH to saponify any ester formed during the reaction gave 4.1 g. V, b3 140-3°, nD25 1.5214. 4,7-Dimethyl-1-indanone (XIII) (10 g.) reduced with LiAlH4 gave 8.5 g. 4,7-dimethyl-1-indanol (XIV), colorless needles, m. 68°. Distn. of the crude XIV obtained from 80 g. XIII and 7.5 g. LiAlH4 gave 58 g. (81%) 4,7-dimethylindene (XV), b3 72-8°, b1.7 63-5°, nD25 1.5583, turned yellow on standing. XV (25 g.), 100 cc. Me2CO, and 10 g. 30% KOH in MeOH refluxed 3 h. and poured into H2O gave mesityl oxide, 19.5 g. XV, and 3.6 g. α,α,4,7-tetramethyl-1- indanmethanol, light yellow oil, b2 135-40°, b1.6 125-8°, nD25 1.5473. XV (6 g.) and 6.6 g. freshly distd. BzH warmed with KOH in MeOH gave 3-phenyl-4,7-dimethylbenzofulvene, yellow needles, m. 65° (from MeOH) in almost quant. yield. 2,5-Me2C6H3CH2CN, b1.7 88-90° (prepd. in 92% yield from 1,4-Me2C6H3CH2Cl by refluxing with KCN in aq. EtOH) (72.5 g.) in 250 cc. dry PhMe was treated with 19.5 g. NaNH2, the mixt. heated 12 h. with stirring, 61.5 g. iso-PrBr added to the refluxing mixt. refluxing continued another 6 h., and the mixt. decompd. with H2O gave 67 g. (71%) 2,5-Me2C6H3CH(CHMe2)CN (XVI), b1.7 97-102°, nD25 1.5088. XVI (46 g.), 400 cc. (CH2OH)2, 40 cc. H2O, and 90 g. KOH were refluxed 30-60 h. until the evolution of NH3 ceased while most of the H2O distd. off, much of the glycol was then removed in vacuo, the residue distd. with H2O, acidified, filtered hot, the filter residue air-dried and extd. with three 250-cc. portions of hot C6H6, the C6H6 removed, and the residue recrystd. from ligroine to yield 41.7 g. (82%) 2,5-Me2C6H3CH(CHMe)CO2H (XVII), needles, m. 126.5-7° (from petr. ether); in AmOH only 15% XVII was obtained because of incomplete hydrolysis at the lower temp., the product being mainly the amide of XVII, white needles, m. 175.5° (from C6H6). XVII (25 g.) and 25 g. SOCl2 warmed on a steam bath 1 h. and let stand overnight gave 23.5 g. 2,5-Me2C6H3CH(CHMe2)COCl (XVIII), slightly colored liq., b2 95-101°. To CH2N2 (prepd. from 45 g. HZNCON(NO)Me in 50 cc. dry Et2O) was added 15.6 g. XVIII, and the Et2O removed after 12 h. to give 16 g. 2,5-Me2C6H3CH(CHMe2)COCHN2 (XIX), yellow crystals. To 7.5 g. XIX in 12 cc. dioxane warmed on a steam bath was added gradually 15 cc. concd. NH4OH and 3 cc. 10% aq. AgNO3, and the mixt. dild. after 1 h. with H2O to give 2.1 g. (85%) amide of V, m. 116-17°. To 9.5 g. LiAlH4 in 250 cc. dry Et2O was added dropwise 40.5 g. XVII in 350 cc. Et2O, and the mixt. stirred 1 h., and decompd. with H2O and 200 cc. 10% H2SO4 to yield 32.5 g. (85%) 2,5-Me2C6H3CH(CHMe2)CH2OH(XX), b2 105-8°, nD25 1.5150. To 19.3 g. XX was added dropwise 13.6 PBr3, and the mixt. heated 2 h. on a steam bath, poured into ice water, stirred, and extd. with Et2O to give 21.5 g. (84%), 2,5-Me2C6H3CH2CHBrCHMe2, b2 112-15°, nD25

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1.5310, giving in an attempted Grignard reaction, followed by carbonation, an unsatd. mobile compd., b1 60-2°, nD23 1.5013, and a viscous material, b2 150-85°, not further investigated.

IT 854876-35-0P, Cinnamic acid, α-cyano-β-isopropyl-2,5-dimethyl-, ethyl ester
RL: PREP (Preparation)
(preparation of)

RN 854876-35-0 CAPLUS
CN Cinnamic acid, α-cyano-β-isopropyl-2,5-dimethyl-, ethyl ester (5CI) (CA INDEX NAME)

L5 ANSWER 129 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1953:25326 CAPLUS
DOCUMENT NUMBER: 47:25326
ORIGINAL REFERENCE NO.: 47:4313c-i,4314a-h
TITLE: Terpenes. XXV. Total synthesis of S-guaiazulene
AUTHOR(S): Sorm, F.; Gut, J.; Hlavnicka, J.; Kucera, J.; Sedivy, L.
CORPORATE SOURCE: Central Chem. Research Inst., Prague
SOURCE: Collection of Czechoslovak Chemical Communications (1951), 16, 168-83
CODEN: CCCCAK; ISSN: 0010-0765
DOCUMENT TYPE: Journal
LANGUAGE: English

GI For diagram(s), see printed CA Issue.

AB 3,4-(MeO)2C6H3CHO heated in MeOH with 10% HCl and Zn-Hg gave, after steam distillation, about 70% 3,4-(MeO)2C6H3Me, b7 102-4°, m. 22.5°, converted into 2,4,5-Me(MeO)2C6H2CHO (I) by the Gatterman reaction. I (60 g.), 39.6 g. NCCH2CO2Et, 100 ml. EtOH, and 1 ml. piperidine at room temperature gave 98% 2,4,5-Me(MeO)2C6H2CH:C(CN)CO2Et, yellow needles, m. 147° hydrogenated with PtO2 in absolute alc. at atmospheric pressure to 92.5% (crude) 2,4,5-Me(MeO)2C6H2CH2CH(CN)CO2Et (II), viscous oil decomposing on attempted distillation in high vacuum. Refluxing 27.7 g. II in glacial AcOH 8 hrs. with 36% H2SO4 followed by partial neutralization, distillation in vacuo (to remove AcOH), addition of H2O, and extraction with C6H6 gave 14.3 g. 2,4,5-Me(MeO)2C6H2CH2CH2CO2H (III), m. 84°, also formed in 74% yield by refluxing II in EtOH with HCl, or by treating crude 2,4,5-(Me)(MeO)2C6H2CH:CHCO2H (IV) with 3% Na-Hg followed by HCl (yield not given). IV, m. 187°, was prepared by heating 50 g. I with 32 g. CH2(CO2H)2 in 50 ml. pyridine and 10 drops piperidine, followed by distillation, solution of the still residue in 5% NaOH, and extraction with Et2O. III (20.4 g.) in 250 ml. C6H6 was freed from the last traces of H2O by distilling off 50 cc., then treated gradually with 90 g. P2O5, refluxed 3 hrs., poured on ice, the pH adjusted to 10, and the product extracted with C6H6, giving 10.5 g. 4-methyl-6,7-dimethoxy-1-indanone (V), C12H14O3, b0.2 131-9° m. 121-2° (from petr. ether), which with MeMgBr gave a nearly quant. yield of the 1,4-dimethyl-6,7-dimethoxy-1-indanol, b2 140°. This, with KHSO4 at 180° for 10 min., gave the dimer (VI), which when distilled at 0.2 mm. gave 82% of the monomer, 1,4-dimethyl-6,7-dimethoxyindene (VIa), yellow oil, b0.2 106°. VIa hydrogenated in AcOH-EtOH with PtO2 gave almost quantitatively the indan, C13H18O2, b0.4 110° m. 43°. This, refluxed 6 hrs. with AcOH and HBr, gave 95% 3,7-dimethyl-4,5-indandiol (VII), b0.5 134° m. 57°. Attempted hydrogenation of the aromatic portion of VII presented difficulties. When PtO2 in glacial AcOH was used, 4 mols. H2 were taken up and the reduction of the ring was accompanied by quant. hydrogenolysis of 1 OH group. An attempt to suppress hydrogenolysis by using Ni-on-kieselguhr and shaking VII in EtOH 8 hrs. with H at 140 atmospheric at 175°, followed by chromatography on Al2O3, gave as 2 main fractions the hydrogenolysis product, C11H20O, b0.5 87-90° (also given as 80-90°), and a sterically individual diol, C11H20O2 (VIII), b0.5 107-8°, m. 76-78°. When, in the hydrogenation of 10.2 g. VII in EtOH, at 110-20° and 185 atmospheric, Raney Ni was used, very little hydrogenolysis resulted and the products were 7.75 g. diol (IX), C11H20O2, m. 99° (from Et2O) and 2.21 g. isomeric diol (X), m. 118° (from Et2O). VIII in AcOH treated with Pb(OAc)4

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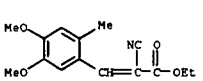
in CHCl3 at 50° the mixt. poured into H2O, extd. with Et2O, the extd. evapd., the residue treated briefly in the cold with KMnO4 in glacial AcOH, poured into H2O, and the mixt. decolorized with Na2S2O3 and extd. with ether yielded 40% HO2CCH2CHMeCH.CH2.CH2.CHMe.CHCO2H (XI), m. 129-30°. When the oxidation of IX was carried out in the dark with HIO4 in EtOH, followed by post-oxidation with KMnO4, 82% of an isomer of XI, prisms, m. 126° (from H2O), was formed. Similarly X on HIO4-KMnO4 oxidation gave 83% of another isomer of XI, m. 121°. Mixed m.ps. of the 2 last isomers showed their nonidentity. XI (0.5 g.) was converted with SOCl2 into the corresponding acid chloride which was added in Et2O dropwise to CH2N2 giving a diazo ketone (XII). This, after evapn. of the Et2O, was dissolved immediately in EtOH and refluxed 3 hrs. with 0.15 g. AgNO3 (with more AgNO3 added at hourly intervals), and the crude ester chromatographed on Al2O3, giving 0.31 g. Et2O2CCH2CH2 CHMeCH.CH2.CH2.CHMe.CHCH2CO2Et (XIII), b0.3 110 11°. Another sample of XII (from 4 g. XI) in 100 ml. dioxane was refluxed 3 hrs. with 50 ml. NH4OH and 1.5 g. AgNO3 in 3 ml. H2O, the evapd. mixt. extd. with hot H2O, and the resulting oily amide hydrolyzed to 0.47 g. of the free dibasic acid (XIV) (corresponding to XIII), m. 104 6°. XIV (4 g.) distd. over the free flame with 4 g. Fe powder and 0.5 g. powd. Ba(OH)2, the distillate shaken in Et2O with aq. NaHCO3, and the ext. evapd. gave by ring closure the crude compd. (XV), which on fractionation yielded 2 main fractions: b12 106-10° (corresponding semicarbazone, m. 206°), and b12 126-36° (semicarbazone, m. 186°) (cf. Plattner and Magyar, C.A. 36, 6514.8). Treated in petr. ether with iso-PrLi, 1.5 g. crude XV gave, after purification by chromatography on Al2O3, 0.48 g. of the compd. (XVI), b9 141°; this (0.6 g.), heated 0.5 hr. at 180° with fused KHSO4, lost H2O, giving 0.46 g. 2,8-dimethyl-5-isopropyl-bicyclo[5.3.0]dec-?-ene, C15H26, b10 122-3°, hydrogenated in EtOH with Adams catalyst to the corresponding bicyclodecane (XVII), C15H28, b10 123°, d420 0.8721, nD20 1.4760. Heated 0.5 hr. to 230° with cryst. S, 0.45 g. XVII gave 0.065 g. S-guaiazulene (XVIII), bright blue, isolated, after chromatography in Et2O on Al2O3, as the trinitrobenzene adduct, black needles, m. 151°, from which XVIII was regenerated by chromatographing. The identity of the synthetic and natural XVIII was also shown by their resp. ultraviolet and infrared absorption spectra. The syntheses clearly indicate that XVIII is 1,4-dimethyl-7-isopropylazulene. 28 references.

IT 58531-10-5P, Cinnamic acid, α-cyano-4,5-dimethoxy-2-methyl-, ethyl ester
RL: PREP (Preparation)
(preparation of)

RN 58531-10-5 CAPLUS

CN 2-Propenoic acid, 2-cyano-3-(4,5-dimethoxy-2-methylphenyl)-, ethyl ester (9CI) (CA INDEX NAME)



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ACCESSION NUMBER: 1951:55473 CAPLUS
DOCUMENT NUMBER: 45:55473
ORIGINAL REFERENCE NO.: 45:9459h-i,9460a-i,9461a-i,9462a-i,9463a-e
TITLE: Formation of nitriles. I
AUTHOR(S): Kurtz, Peter
CORPORATE SOURCE: Farbenfabriken Bayer, Werk Leverkusen, Germany
SOURCE: Ann. (1951), 572, 23-82
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 45:55473

GI For diagram(s), see printed CA Issue.

AB The following members of the research and tech. staffs also contributed materially to this extensive study: W. Lehmann, F. Lober, H. F. Piepenbrink, H. Schwarz, F. Moller, R. Schroter, R. Ludwig, A. Casper, H. Haberland, J. Heinen, D. K.hivin.astner, T. Konig, G. Manz, R. Stroh, H. Wolz, H. Brock, K. Sigwart, and H. Weber. More than 270 literature refs. are given, many of them to German patents, and the following subjects are discussed in a lengthy introduction (pp. 23-52): the addition of HCN (I) to unsatd. esters and nitriles; the formation of esterified α-HO nitriles; the addition of I to unsatd. sulfones and nitro compds.; the addition of I to C2H2 and substituted acetylenes; chemical reactions of NCCH:CHCH:CH2 (II); and the interaction of I with CH2:CHCH2OH and related compds. A number of previously prepared compds. are included (full refs. to which are given in the extensive bibliog.). To 300 g. CH2:CHCN and 3 g. KCN was added (in 1 portion) 1/3 of the equimolar amount of (anhydrous or highly concentrated) I, the mixture warmed to 30°, maintained (after the incipient reaction) at 55-60°, 2/3 of the equimolar amount of I added dropwise (with cooling as required), the mixture warmed 2 h. at 60-70°, and the resulting brown mass was distilled directly in vacuo, giving 420 g. (93%) (CH2CN)2 (III), b10 136°, m. 55°, and 25 g. resinous residue. The above reaction also took place in pyridine (without KCN addition), giving 86%

III. When it was carried out on a large scale, a certain amount of crude III (from prior runs) was kept in the reaction vessel, with fresh KCN added, and both the CH2:CHCN and I added dropwise to the mixture; under these conditions yields of 96% III could be reached. By analogous slightly modified procedures (with either K2CO3 or KCN) the following esters of NCCH2CH2CO2H were prepared from the appropriate CH2:CHCO2R (IV): 73% Me, b11 100-1°; 80% Et, b19 111-12°; 78% Bu, b10 123° (yields based on IV entering the reaction). By thermal degradation, Me2C(OAc)CN gave AcOH and CH2:CMeCN, b760 88-90°, which, refluxed with I (and small amts. of KCN) at 40° gave about 1.8% NCCH2CHMeCN (V), b14 120-30° (hydrolyzed by HCl at 110° to HO2CCH2CHMeCO2H, m. 110-12°). V (5%) was also formed from 40 g. mixed cis- and trans-MeCH:CHCN with 17.5 g. I and 0.3 g. KCN; in 20% yield (b0.5 89-91°) by the action of anhydrous I and KCN on CH2:CHCH2CN, and in 26% yield when I in the last named reaction contained small amts. of H2O. Tech. CH2:CMeCO2Me (90.5 g.) refluxed 15 h. with 26 g. I and 2 g. KCN gave 6 g. NCCH2CHMeCO2Me, b11 90°. MeCH:CHCO2Et (80 g.) by an analogous reaction gave 2 g. (slightly impure) NCCHMeCH2CO2Et, b18 105-10°. Δ3-Tetrahydrobenzonitrile, PhCH:CHCN, and PhCH:CHCO2Et all failed to react with I (and KCN). Pyrolysis of PhCMe(OAc)CN gave the easily polymerized PhC(:CH2)CN, b0.4 74-6°, 10 g. of which with I and KCN gave 7.8 g. PhCH(CN)CH2CN, m. 68-9° (after crystallization from alc. and H2O). MeOCH2CH:CHCN by analogous condensation with I gave MeOCH2CH(CN)CH2CN, b0.1 101-4°. ClCH2CH:CHCN was converted into the AcO analog, b11 96-99°; the

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latter with I and KCN formed small amts. of an undistillable resin. Me2NCH2CH:CHCN, b17 64-66° (picrate, m. 124°), also yielded resinous products and HNMe2. 1-CYano-4-(1-piperidyl)-2-butene (Va), b14 130-1° (picrate, m. 98°), was prepd. by the condensation of piperidine and II; yield 86%. II, b50 58-62°, was formed as follows: I + MeCH:CHCHO →Ac2OH2SO4 76% MeCH:CHCH(CN)OAc, b14 87-92° →500-200°pyrolysis 60-70% II. Va (50 g.) and 9 g. I gave 51% CH2.CH2.CH2.CH2.CH2.NCH2CH2CH(CN)CH2CN, b0.8 146-54°, (picrate, m. 142-44°). Va heated with I and small amts. of KCN gave rise to much polymn., and the expts. were often not reproducible. The mixt. of Va and I heated 6 h. at 45-50° and 10 h. at 65-70° gave very small amts. of (:CHCH2CN)2 (VI), m. 72-3° (from C6H6-petr. ether). In another expt., the mixt. heated 6 h. at 95-100° gave, besides a large resinous residue, a yellow oil, b14 150-80°, which (presumably) contained the isomer NCCH:CH2CH2CH2CN, because on Pd-C catalytic hydrogenation, in MeOH, the mixt. gave an oil, b14 160-70°, which with HCl at room temp. gave (CH2CH2CONH2)2, m. 218-20°. MeCH:CHCH:CHCO2H (prepd. from tech. cyanosorbic acid by decarboxylation) failed to give any definite condensation product with I. Under the usual conditions, HC.tplbond.CCO2Me and I gave 24% NCCH:CHCO2Me; b14 95-7°, m. 35-6° (from Et2O-petr. ether) [readily sapond. to fumaric acid, m. 286-7° (decompn.)]. MeCH:C(CO2Et)2 with I gave 92% MeCH(CN)CH(CO2Et)2, b10 141-3°. On the other hand, PhCH:C(CO2Et)2 (81 g.) and I gave largely the starting material (71.5 g.) and about 10 g. of an uncrystallizable resin contg. 5.45% N (C15H17O4N requires 5.1% N). Di-Me maleate (150 g.) and I gave 33.2 g. of an oil, b0.8 180-184°, which crystd. very gradually but could not be recrystd. and was evidently NC[CH(CO2Me)]3CH2CO2Me; it gave no FeCl3 reaction, was insol. in aq. Na2CO3, and on hydrolysis with HCl at 90° (and finally at 120-30°), followed by evapn. to dryness and heating with Ac2O gave an anhydride, m. 240-42°, which with boiling H2O yielded meso-[HO2CCH2CH(CO2H)]2, m. 188-9°. Condensation of NCCH:CHCH2CN (VII) with I, and extn. of the product with AcOEt, followed by washing with aq. H2SO4 and H2O, drying, and evapn. gave an (unanalyzed) oil (probably an adduct) which decompd. and resinified when heated in a high vacuum. VII (30 g.) on standing 24 h. at room temp. with 65 g. H2SO4 and 210 g. MeOH, followed by heating gradually to 130° and maintaining 4 h., gave after (a fully described) purifn. 37.2 g. di-Me ester of VII, b15 113-14°, 33 g. of which with I (and KCN) gave 3.5 g. (unanalyzed and uncharacterized) NCCH(CH2CO2Me)2 (?), readily sapond. to HO2CCH(CH2CO2H)2, m. 159-60°. From appropriate esters of the type CH2:CHO2CR by addn. of I, the following cyano compds. of the type RCO2CH(CN)Me were prepd. (R is given): 43% H, b15 60-1°; 82% Me, b11 61-2°; 47% Ph, b11 138-40°; and 41% Me2CHCH2CH2, b10 95-6°. MeCH:CHCO2CH:CH2 (150 g.) with 2 g. KCN and 40 g. HCN, yielded 2 compds., sepd. on repeated fractionation: 13.2 g. MeCH:CHCO2CHMe(CN), b11 91-2°, and 34 g. MeCH(CN)CH2CO2CHMe(CN), b0.25 116° (the latter on sapon. forming HO2CCHMeCH2CO2H, m. 110-12°). Compds. of type RCH(OAc)2 or RCH(O2CEt)2 heated at about 140-150° with dry KCN (or NaCN) gave inseparable mixts. of the starting product and the corresponding R'CO2CH(CN)R. Thus from 100 g. MeCH(OAc)2 was formed 67 g. of a mixt. (contg. 8.8% N instead of the theor. 12.38%), b20 73°; from MeCH(O2CEt)2, a mixt. b13 70-2° (contg. 7.35% N instead of 11.02%); from H2C(OAc)2, a mixt. b10 62-66°, contg. AcOCH2CN (10.5% N instead of 14.14%); from Me2CHCH(OAc)2, a mixt., b12 75-77° (contg. 5.3% instead of 9.92% N); PhCH(OAc)2 gave a mixt. contg. PhCH(OAc)CN, b12 131° (which when hydrolyzed with HCl yielded PhCH(OH)CO2H, m. 117-18°). AcOCH:CH2CH:CH2 and I (with KCN), 6 h. at

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95-100°, gave 57% AcOCH(CN)CH:CHMe (or AcOCH(CN)CH2CH:CH2), b20 85-88°. Similarly CH2:C(O2CEt)CH:CH2 yielded much resin and 15% EtCO2CMe(CN)CH:CH2, b14 90-3°. To 6 g. I and 0.5 g. KCN were gradually added 30 g. EtSO2CH:CH2 with the (outer) temp. maintained at 24-32°, during the addn. and then 2 h. at 50°. The reaction product, a viscous oil (presumably EtSO2CH2CH2CN), b0.5 160-8° (partial decompn.), was never obtained pure (KCN, admixed with EtSO2CH:CH2 induced rapid exothermic polymn.). By heating 27 g. O2S.CH2.CH2.CH:CH with 1 g. KCN and 8 g. I, 16 h. at 35-40°, SO2.CH2.CH2.CH(CN).CH2, m. 118°, was formed. O2S.CH2.CH:CH.CH2 apparently does not add I. [p-MeC6H4SO2CH:CH2, however, formed 71% MeC6H4CH2CH2CN, m. 94-5°.] PrCH:CHNO2 added HCN, forming the pale yellow PrCH(CN)CH2NO2, oil, b14 133-5° (the yield of which could not be detd., because of an explosion occurring after about 1/3 of the crude product had been distd.). The following method was adopted for the prepn. of CH2:CHCN (VIII): Into a well-stirred mixt. of 300 g. Cu2Cl2, 100 g. NH4Cl, 5 cc. concd. HCl, 200 cc. H2O, and small amts. of Cu powder at 90° was gradually introduced over 3.5 h. a mixt. of 60-70 l. C2H2 and 20 g. I. The yields of VIII (purified by fractionation) varied from 32 to 88%, but the contact soln. remained active for at least 14 successive runs. (The highest yield of VIII was obtained in the 14th run). VIII was fully identified by the formation of several derivs. (not analyzed), including conversion into III. The still residues (about 600 g.) from the various prepns. of VIII were fractionated in vacuo; of these 289 g. (b30 below 35°) was largely VIII. A fraction b30 35 to b15 80° (48 g.) when steam-distd., Et2O-extd., and fractionated gave 5 g. II, b38 54-59° (identified through the picrate of Va m. 98°) and in the residue from the steam distillate, MeCH(OH)CN, b14 80-90°. Chloroprene was also probably present as an impurity in crude VIII. The following consts. of VIII were detd.: b760 77.6-7.7°, heat of combustion 415.8 kcals./mol, heat of vaporization 0.136 kcals./g. The vapor pressures of VIII (at temps. from -16° to 78.8°) were detd., as were the solubilities of VIII in H2O (at -20 to 84°) and of H2O in VIII (at 0° to 66°) (data for which are tabulated). To a contact mixt. of 1100 g. Cu2Cl2, 590 g. NH4Cl, 950 cc. H2O, 25 cc. HCl, and 30 g. Cu powder at 80° was added dropwise a mixt. of 44 g. CH2:CHC.tplbond.CH and 40 g. HCN. The temp. of the mixt. rose to 50° (after 5 h.); the mixt. was kept at this temp. 10 h., then warmed further by means of a gentle N stream, the condensate extd. with Et2O, and the ext. washed, dried, and fractionated, giving 11.7 g. (17%) II, b44 56-60° (identified as picrate of Va, m. 98°). By an analogous reaction, with a similar contact agent, 160 g. PhC.tplbond.CH gave 1.5 g. (impure) PhCH:CHCN, b12 115-35° (hydrolyzed to PhCH:CHCO2H). Heating 20 g. II and 21 g. H2C:CMeCMe:CH2 [stabilized with p-C6H4(OH)2] 1 h. at 140° gave 19 g. of an adduct, C11H15N, b1.5 82-7°. Similarly 27 g. II and 30 g. chloroprene at 100° gave 7 g. of an adduct, C9H10NCl, b13 141-51°. Dropwise addn. of 100 g. II to 140 g. MeOH contg. MeONa (from 2 g. Na) at 50-60° gave 39% MeOCH2CH2CH(OMe)CH2CN, b17 109-11°, which, hydrogenated in MeOH contg. NH3, with Raney Ni at 110 atm. pressure, gave 85% MeOCH2CH2CH(OMe)CH2CH2NH2, b15 87-91°, giving no cryst. Bz deriv. or picrate. II (100 g.) in 500 cc. MeOH satd. with NH3, let stand 6 days at room temp., and evapd., gave a viscous pale brown oil (H2O-sol.), decompg. on distn., contg. about 22.85% N (possibly C15H18N4). II (100 g.) in 50 cc. THF and 250 cc. liq. NH3, hydrogenated in the presence of Ni-fuller's earth at 70-120°, gave, after fractionation, 24 g. (slightly impure) HZN(CH2)4CN, b12 92-3°; Bz deriv., m. 57-9°. With Raney Ni as catalyst, II in THF and liq. NH3 hydrogenated gave a large amt. of resin, some AmNH2, and 6 g. HZN(CH2)5NH2, b12 75-80° (di-Bz deriv., m.

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130-31°). II (50 g.) added rapidly to 170 g. 50% aq. EtNH2 and heated 5 h. at 50° gave 48.6 g. of a liq., b12 120-24° (slight decompn.), contg. about 23.3% N (presumably a mixt. of C7H12N2 and C9H19N3) and 31.7% of a dark resin. From aq. Me2NH (400 g. 48% soln.) and 216 g. II at 80° was formed an oily mixt., which, when extd., distd., and retreated with 300 g. Me2NH soln., yielded 217 g. Me2NCH2CH2CH(NMe2)CH2CN (IX), b10 120-22° (picrate, m. 122-3°). By a slightly modified procedure, 100 g. II gave, besides IX, 67.6 g. Me2NCH2CH:CHCH2CN, b15 86-96°, which, hydrogenated in NH3-MeOH (with Ni and fuller's earth), yielded Me2N(CH2)5NH2 (Au salt, m. 168°). Et2NH (in excess) reacted vigorously with II, giving as the only product 81% Et2NCH2CH:CHCH2CN (X), b15 107-14° (picrate, m. 96°), which when heated in a bomb tube at 120-30° decompd. and resinified. X hydrogenated with Pd-C gave Et2N(CH2)4CN, b15 108-12° (picrate, m. 86-8°). On more vigorous hydrogenation (with Ni-fuller's earth) X in NH3-MeOH at 90-120° gave Et2N(CH2)5NH2 (XI), b14 95-8° (picrate, m. 129-30°); p-O2NC6H4CO deriv., m. 84-4.5° (from petr. ether). The constitution of the adduct X was indicated by the following synthesis of XI: 1-benzoylpiperidine →PCl3BzNH(CH2)5Cl →Et2NH BzNH(CH2)5NEt2 →HCl bomb tubeXI. II with N2H4.H2O in MeOH (with cooling) gave in good yield H2NNHCH2CH:CHCH2CN, b4.5 131-5° (Bz deriv., m. 231-2°). Similarly II and Me2NNH2 gave Me2NNHCH2CH:CHCH2CN, b12 110-17°. To 50 g. II and 1.5 g. Na2S at 60-70° was added in a rapid stream 11.5 g. H2S, yielding a viscous oil, which, dissolved in C6H6, washed successively with aq. H2SO4 and H2O and freed from C6H6 in vacuo, gave (nearly pure) (NCCH2CH:CHCH2)2S (XII), decompg. on attempted fractionation; when heated 5 h. with concd. HCl, it gave a mixt. of stereoisomeric unsatd. dicarboxylic acids, C10H14O4S, m. 152-5°. To 60 g. HSCH2CO2Et and 0.5 g. KOH at 70° was added dropwise 44 g. II, and the product, purified like XII, gave 11.4 g. NCCH2CH:CHCH2SCH2CO2Et, b0.3 136-40°. II and an aq. 30% soln. of NaHSO3 at 90-100° gradually reacted to form NaO3SCH2CH:CHCH2CN (pptd. from the aq. mixt. with MeOH-Et2O); this with Raney Ni in MeOH gave an (uncharacterized) cryst. compd., which with BzCl gave BzNH(CH2)5SO3Na, m. 216-17° (from MeOH). CH2:CHCH2OH (72%)(29 g.) and 14 g. I, 4.5 g. Cu2Cl2, and 2.6 g. NH4Cl, heated 16 h. in a bomb tube at 95-100°, failed to give an adduct, but yielded 23.3 g. CH2:CHCH2CN, b. 114-16°. PhCH2OH treated similarly (but with NH4Br and Cu2Br2 as catalysts) gave no adduct, and formed very little PhCH2CN, the principal product being (PhCH2)2O, b18 160-65°. To a stirred mixt. of 200 g. Cu2Cl2, 150 g. KCl, and 172 cc. H2O, made acid to Congo red and treated with Cu powder, were added over a 6-h. period 352 g. (HOCH2CH:)2 and 224 g. I at 80°, stirring continued 2 h. longer, and the mixt. extd. at 60° with C6H6 and fractionated, yielding as the main (68%) fraction 293 g. crude VI, and 38 g. resin. The contact mixt., after evapn. of the H2O, was reused in subsequent runs (giving 74-75% VI). Purified VI, m. 76° (from EtOH), d804 0.953, heat of combustion 811.8 kcals./mol, heat of vaporization, 0.1144 kcals./g. (at 274°, 760 mm.). Sp. heat and solubilities in MePh, xylene, PhCl, EtOH, and H2O (at various temps.) were detd. In the recrystn. of VI, the mother liquors yielded an oily mixt., apparently contg. HOCH2CH:CHCH2CN, or an isomer, inasmuch as hydrogenation in NH4OH with Raney-Co gave H2N(CH2)5OH, b13 114-15°, m. 38° (picrate, m. 94-5°). With Raney-Ni, VI in THF contg. NH3 was hydrogenated to 85% (CH2CH2CH2NH2)2, m. 38-9° (di-Ac deriv., m. 123-4°; di-Bz deriv., m. 157-8°). The action of Cu2Cl2 on VI (at 150° and 200° for 5 h.) with varying amts. of catalyst was studied exhaustively. In general, the lower the

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temp., and the lower the % catalyst, the less decompn. (i.e., resin formation) of VI was noted. E.g., at 150°, with 1% Cu2Cl2, VI was completely resinified; with 0.01% Cu2Cl2 at 150°, it was almost quant. recovered; at 200°, it isomerized and/or resinified, unless the catalyst was reduced to 0.01%. (Details are given for removal of residual Cu2Cl2.) When 1 kg. VI and 1 g. Cu2Cl2 were heated 5 h. at 200° and the cooled mixt. extd. with C6H6, filtered, and freed from solvent, the residue (869.5 g.) failed to crystallize and on distn. yielded 2 main fractions, each of which had the compn. C6H6N2 (apparently the cis- and trans-isomers of NCCH:CHCH2CH2CN), b0.9 108-12°, n20D 1.46777, and b0.9 115-118°, n20D 1.46865, together with 116 g. resin. Crude VI with 10% aq. KCN resinified. Various relatively unsatisfactory methods for prepg. VI are outlined. E.g., 300 g. (HOCH2CH:)2 and 95 g. I added slowly to 200 g. Cu2Cl2, 162 g. NH4Cl, 172 cc. H2O, 5 cc. HCl, and 15 g. EtOH, and the mixt. extd. with C6H6 and fractionated gave 61.3 g. EtOCH2CH:CHCH2CN, b12 90-104°, and 60.4 g. VI. To 650 g. Cu2Cl2, 350 g. NH4Cl, 500 cc. H2O, 10 g. Cu powder, and 30 cc. HCl in an atm. of N at 105-110° was added 1 kg. CH2:CHCH2OH at the rate of 100-200 cc./h., and the resulting products promptly distd., extd. with CH2Cl2, and fractionated in a Raschigring column, giving 650 g. (CH2:CHCH2)2O, b. 89.5-91.5°. Very similarly formed were (PhCH2)2O, b14 164-6°, and (by successive addns. of BuOH and allyl alc. to the catalyst) CH2:CHCH2OBu, b. 114-18°; (from (CH2OH)2 and allyl alc.) (CH2:CHCH2OCH2)2, b18 60.5-4°; and [from (HOCH2CH2)2 and allyl alc.], (CH2:CHCH2OCH2CH2)2, b10 84-7°.

IT 1615-70-9, 2,4-Pentadienenitrile
(and adducts)

RN 1615-70-9 CAPLUS

CN 2,4-Pentadienenitrile (CA INDEX NAME)

IT 13042-02-9, α-Hydromuconononitrile
(mixture containing)

RN 13042-02-9 CAPLUS

CN 2-Hexenedinitrile (CA INDEX NAME)

IT 107-13-1P, Acrylonitrile 126-98-7P, Methacrylonitrile 495-10-3P, Atroponitrile 2141-59-5P, α-Hydromuconononitrile, trans- 4360-47-8P, Cinnamonitrile 44653-08-9P, Acrylic acid, 3-cyano-, methyl ester 90330-08-8P, Crotononitrile, 4-hydroxy-, acetate 101084-47-3P, Crotononitrile, 4-dimethylamino- 856181-87-8P, Crotononitrile, 4-dimethylamino-, picrate
RL: PREP (Preparation)
(preparation of)

RN 107-13-1 CAPLUS

CN 2-Propenenitrile (CA INDEX NAME)

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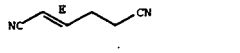
RN 126-98-7 CAPLUS
CN 2-Propenenitrile, 2-methyl- (CA INDEX NAME)

RN 495-10-3 CAPLUS
CN Benzeneacetonitrile, α-methylene- (CA INDEX NAME)

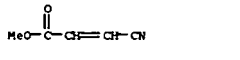
RN 2141-59-5 CAPLUS
CN 2-Hexenedinitrile, (2E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.

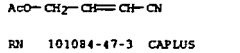


RN 4360-47-8 CAPLUS
CN 2-Propenenitrile, 3-phenyl- (CA INDEX NAME)

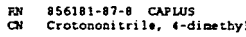
RN 44653-08-9 CAPLUS
CN 2-Propenoic acid, 3-cyano-, methyl ester (CA INDEX NAME)



RN 90330-08-8 CAPLUS
CN 2-Butenenitrile, 4-(acetyloxy)- (9CI) (CA INDEX NAME)



RN 101084-47-3 CAPLUS
CN 2-Butenenitrile, 4-(dimethylamino)- (9CI) (CA INDEX NAME)



RN 856181-87-8 CAPLUS
CN Crotononitrile, 4-dimethylamino-, picrate (5CI) (CA INDEX NAME)

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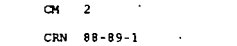
CM 1

CRN 101084-47-3
CMF C6 H10 N2



CM 2

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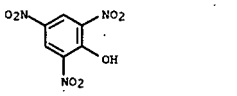
CMF C6 H3 N3 O7



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ACCESSION NUMBER: 1951:8765 CAPLUS
DOCUMENT NUMBER: 45:8765
ORIGINAL REFERENCE NO.: 45:1589f-i,1590a-i,1591a-i,1592a
TITLE: Piperidine and azabicyclo compounds. I. Via Michael condensations
AUTHOR(S): Albertson, Noel F.
CORPORATE SOURCE: Sterling-Winthrop Research Inst., Rensselaer, NY
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GI For diagram(s), see printed CA Issue.

AB Since so many piperidine compds. show marked physiol. activity, their synthesis, by catalytic reduction to piperidines and bicyclo N compds. of δ-keto nitriles prepared by Michael condensations between vinyl ketones and cyanoacetic esters or between CH2:CHCN (I) and β-ketones, was reinvestigated. Adding 600 mL. AcCH2CO2Et (II) to 3 g. Na in 400 mL. EtOH, followed by 246 mL. I at such a rate that the temperature did not exceed 45°, distilling off the EtOH, washing the residue with H2O containing 10 mL. AcOH, and distilling gave 63% AcCH(CO2Et)(CH2)2CN (III), b2 121°, n25D 1.4446, and a residue of AcC(CO2Et)(CH2CH2CN)2 (C.A. 23,834). Adding 200 g. III to 200 g. Na2CO3 in 1800 mL. H2O, refluxing 4 h., salting out with K2CO3, and extracting with Et2O gave 71% Ac(CH2)3CN (IV), b5.2 86.5°, n25D 1.4790 (2,4-dinitrophenylhydrazone, m. 154-5°). IV may also be prepared from I and Me2CO, but the yield is very low (8.6%) because of polycyanoethylation. β-Keto esters give much higher yields of (CH2)2CN derivs. than do ketones. Reduction of IV with Raney Ni gave 85% MeC.(CH2)4.NH. Addition of 168 g. AcCH(CH2Ph)CO2Et (V) to 0.5 g. Na in 200 mL. 95% EtOH, followed by 53 mL. I at such a rate that the temperature remained at 25-35°, acidification with alc. HCl 0.5 h. after the addition of I, and distillation gave 141 g. (85%) AcC(CH2Ph)(CO2Et)(CH2)2CN, b1.5 172°, n25D 1.5068, and 35 g. V. Use of com. absolute EtOH gave PhCH2CH(CO2Et)(CH2)2CN, b2.0 152°, n25D 1.5002, as major or sole product by loss of an Ac group. Addition of 512 g. CH2.CH2.CHAc.CO.O to 2 g. Na in 300 mL. EtOH, followed by 290 mL. I, acidification of the mixture after 1 h., and allowing to stand 1-2 days gave 86-92% CH2.CH2.CAc(CH2CH2CN).CO.O (VI), m. 44-6° (from MeOH), b1.5 162°, n25D 1.4790, which on refluxing 6 h. with 10% aqueous Na2CO3, salting out with K2CO3, extracting with iso-PrOH, and distilling gave a poor yield of yellow oil, b3.5 115-46° [2,4-dinitrophenylhydrazone, m. 159° (from AcOEt)]. VI (40 g.) hydrolyzed by 80 g. KOH in aqueous MeOH, acidified, extracted with AcOEt, and concentrated gave 22 g. α-(2-hydroxyethyl)glutaric acid lactone, b1.0 163-6°. BzCH(CO2Et)(CH2)2CN (VII) (100 g.), refluxed 10 h. with 100 g. Na2CO3 and 900 mL. H2O, extracted with Et2O, dried, and distilled gave 37.0 g. (52%) Bz(CH2)3CN, b0.1 125°, n25D 1.5326, and 4 g. Bz(CH2)3CONH2 (VIII), m. 140-1° (from H2O). VIII was also prepared by condensing I with AcCHBzCO2Et and hydrolyzing the condensation product with Na2CO3 solution Addition of 122 g. III and 50 mL. MeI to 15.3 g. Na in 300 mL. dry EtOH and working up the mixture in the usual manner after 2 days' standing gave, on distillation, 35.6 g. NC(CH2)2CHMeCO2Et, b0.8 74-80°, n25D 1.4270, and 63.6 g. AcCMe(CO2Et)(CH2)2CN, b0.8 109°, n25D 1.4461. AcC(CHMe2)(CO2Et)(CH2)2CN, b0.1 121° n25D 1.4542, was prepd. in 37% yield by the method of Koelsch and Walker (C.A. 45, 1135f) and in poorer yield from III, iso-Pr2O, and BF3 by the method used by Hauser and Breslow (C.A. 34, 7875.6) to alkylate II. Other keto nitriles, AcCRR'CH2CH2CN, prepd. in a manner analogous to III: (R, R', yield (%), b.p. °C. (mm.), n25D resp., given): CH2CH2CO2Me, CO2Et, 100, 166° (1.7), 1.4510; CH2CH2CO2Et, CO2Et, 82, 168° (0.8), 1.4578; CH2Ph, CO2Me, 56, 163° (0.2), 1.5158; C6H13, CO2Et, 73, 157° (2.9), 1.4511; C7H15, CO2Et, 81, 145° (0.9), 1.4505; iso-Bu, CO2Et, 60, 125° (0.1), 1.4528. Also prepd. were CO.CH2.CH2.CH2.C(CO2Et)(CH2)2CN, 82, 145° (1.5), 1.4663; AcC(CH2CH2CN).CH2.C(CH2Cl).O.CO, 61, 199° (1.6), 1.4982; and BzCH(CO2Et)(CH2)2CN, 86, 176° (0.7), 1.5131. AcC(CH2OH)(CO2Et)(CH2)2CN, n25D 1.4585, was obtained in 94% yield from IV and formalin. Redn. of 93 g. AcC(CO2Et)(CH2CH2CO2Me)(CH2)2CN in 400 mL. EtOH by Raney Ni and H at 100° and 50 lb. pressure for 6 h., removal of the EtOH in vacuo, and filtration from dil. Et2O gave 36% 5-carbethoxy-9-methyl-2-oxo-1-azabicyclo[3.3.1]nonane, m. 170.4-1.3° (cor., from EtOH). The Et2O soln. gave 37.9 g. (43%) Et 3-(2-carbomethoxyethyl)-2-methylnipecotate, b1.4 139°, n25D 1.4740. A soln. of 115 g. Et 2-(2-cyanoethyl)cyclopentan-1-one-2-carboxylate in 400 mL. EtOH reduced by Raney Ni and H at 120° and 400 lb. pressure for 7 h. gave, on distn., 79 g. (73%) 4a-carbethoxyoctahydro-1-pyrindine (IX), b0.6 87°, n25D 1.4799 (cf. Henecka, Fr. 881,360), and 14.7 g. of a yellow oil, b0.4 153-209°, n25D 1.4852-8, m. 52.9-4.8° (cor., from Et2O), which may be the alc. obtained by redn. of the C:O bond. Redn. of 1 mol VI in 400 mL. MeOH by Raney Ni and H at 90° and 500 lb. pressure for 6 h. and treatment of the product with alc. HCl gave 62 g. 1-methyl-2-aza-8-oxaspiro[5.4]decan-7-one-HCl (X), m. 265-6.4° (cor., from EtOH). Hydrogenation of 116.2 g. Et 2-methylnipecotate in 400 mL. EtOH and 68 mL. 37% formalin at 25° and 400 lb. pressure with a buffered Pd-C catalyst required less than 45 min., giving on distn. 122.2 g. (98%) Et 1,2-dimethylnipecotate (XI), b0.2 73°, n25D 1.4557 [methiodide, m. 185.0-6.4° (cor.)]. The following piperidines (Xa) were prepd. in a similar fashion (R1, R2, R3, R4, % yield, b.p. °C. (mm.), n25D, resp.): H, Me, H, H, 85, 117° (760), 1.444; H, Me, H, CO2Et, 86, 59° (0.5), 1.4557 [1-PhNHCO deriv., m. 134.6-6.0° (cor.)]; Me, Me, H, CO2H, -, - (-), - [HCl salt, m. 185.8-8° (cor.)]; H, Me, Me, CO2Et, 89, 63° (0.1), 1.4581 [HCl salt, m. 164.4-5.0° (cor.)]; Me, Me, Me, CO2Et, 58, 67° (0.9), 1.4592; H, Me, iso-Pr, CO2Et, 84, 91° (0.3), 1.4666; Me, Me, iso-Pr, CO2Et, 82, 92° (0.6), 1.4642; H, Me, iso-Bu, CO2Et, 91, 98° (0.3), 1.4658; Me, Me, iso-Bu, CO2Et, 84, 95° (0.9), 1.4612; H, Me, C6H13, CO2Et, 85, 106° (0.2), 1.4627; Me, Me, C6H13, CO2Et, 80, 130° (1.9), 1.4609; H, Me, C7H15, CO2Et, 63, 120° (0.7), 1.4665; Me, Me, C7H15, CO2Et, 33, 136° (1.5), 1.4638; Me, Me, PhCH2, CO2Et, 81, 134° (0.2), 1.5110; H, Me, PhCH2, CO2Me, 78, 137° (0.6), 1.5335; Me, Me, PhCH2, CO2Me, 75, 132° (0.8), 1.5223; H, Me, Ph, CO2Et, 57, 131° (0.3), 1.5323; H, Me, -(CH2)2CO-, 30, - (-), - [HCl salt, m. 265-6°]; Me, Me, -(CH2)2CO-, 70, - (-), - [HCl salt, m. 72-5°]; Me, -(CH2)3-, CO2Et, 85, 83° (1.0), 1.4755; H, Me, (CH2)2CO2Et, CO2Et, 65, 133° (0.9), 1.4740; Me, Me, (CH2)2CO2Et, CO2Et, 86, 128° (1.0), 1.4726; H, Me, (CH2)3NH2, Me, 77, 80° (1.2), 1.5031 (b760 250-5°); di-HCl salt, m. 243-6°; monopicrate, m. 194-5°); H, Ph, H, H, 80, 80° (0.2), 1.5232 (readily hydrated on shaking with H2O); Me, Ph, H, CO2Et, 94, 116° (0.1), 1.5178. Redn. of 90 g. III in 400 mL. EtOH by Raney Ni and H at 60° and 600 lb. pressure for 1-3 h./mol H gave 89-93% 5-carbethoxy-6-methyltetrahydro-2-pyronimine, b0.9 103-6°, n25D 1.5350 (supercooled, solid at room temp.), which loses NH3 on refluxing with HCl and is undoubtedly identical with Henecka's 1-cyanopentan-4-ol-3-carboxylic ester (C.A. 44, 2520c). Redn. of γ-cyano esters with Raney Ni gave only piperidines, usually in high yield, while redn. of III gave 86% XI. These results are in marked contrast to those of Henecka (see above), who stated that III does not give a piperidine on redn. unless first converted to the corresponding β-aminocrotonic ester with NH3. Redn. of 165 g. VII in 335 mL. EtOH with Raney Ni and H at 115° and 700 lb. pressure for 1 h. and distn. gave 113.1 g. (73%) Et 2-phenylnipecotate, b0.08 113°, n25D 1.5227 [HCl salt, m. 202.2-3.4° (cor.); phosphate, m. 183.3-4.9° (cor.)], some BzH, and 19.3 g. of an oil depositing crystals of 5-carbethoxy-6-phenyltetrahydro-2-pyronimine, m. 106.2-8.4° (cor.) (from petr. ether, AcOEt, and iso-PrOH successively). 4-(2,3-Dimethoxyphenyl)-3-buten-2-one (XII), b1.1 135-9°, n25D, 1.5810 (70% yield), and AcCH2CHPhCH(CN)CO2Et, b0.8 160-5°, n25D 1.5102, were prepd. in the usual manner. Addn. of CH(CN)EtCO2Et (XIII) to PhCH:CHAc gave 23% AcCH2CHPhCEt(CN)CO2Et, b1.4 153-61° (decompn.), n25D 1.5050. A soln. of 103 g. XII and 71 g. XIII in 100 mL. EtOH, just basic to EtONa, warmed 2.5 h. on a steam bath, acidified with alc. HCl, concd., and distd. gave 129 g. of an oil, b1.5 55-151°, which on treatment with EtONa and 3 days' standing gave 96.5 g. Et 2-cyano-2-ethyl-3-(2,3-dimethoxyphenyl)-5-oxohexanoate, b1.5-2.4 160-97°, n25D 1.5168 (supercooled), m. 91-4° (from EtOH). Octahydro-4-methyl-1H-quinolizine(?) (HCl salt, m. above 360°; cf. Lukes and Sorm, C.A. 42, 7780d) and 1-(2-piperidyl)-4-pentanol were prepd. by redn. of 1-(2-pyridyl)-4-pentanone by Raney Ni and H at 150° and 250 lb. pressure (Boekelheide and Rothchild, C.A. 43, 4267e). AcCH2Ac (50 g.), 1.5 g. Na, and 108 g. 2-vinylpyridine refluxed 7 h. and distd. gave 14.1 g. 1-(2-pyridyl)-4-pentanone (XIV), b1 84-118°, and 37.4 g. of the 3-Ac deriv. of XIV, b1 118-19°. The following piperidines (XV) were prepd. by the Raney Ni redn. of the keto nitriles in EtOH or by reductive methylation of the piperidines with formalin and a Pd-C catalyst as previously described (R1, R2, R3, b.p. (mm.), n25D, resp.): H, H, Ph, 130° (1.0), 1.5172; Me, H, Ph, 127° (1.5), 1.5104; H, Et, Ph, 131° (1.6), 1.5148; Me,Et, Ph, 118° (0.6), 1.5105; H, Et, 2,3-(MeO)2C6H3, 158° (0.8), 1.5194; Me, Et, 2,3-(MeO)2C6H3, 153° (0.9), 1.5152. Whereas redn. of α-(2-cyanoethyl)acetoacetic esters gave principally piperidines, redn. of Et α-[2-(2-pyridyl)ethyl]acetoacetate in EtOH with Raney Ni at 150° gave 40% Et octahydro-4-methyl-1H-quinolizine-3-carboxylate and 45% octahydro-3-(1-hydroxyethyl)-4-oxo-4H-quinolizine, the piperidone type of ring closure predominating. Of the mols. having more than 1 asym. C atom, only a single dl-modification is obtained on redn. Nearly all these piperidines and bicyclo compds. have been prepd. in only 3 steps from readily available and cheap materials. Some of these compds. show mild analgesic activity.

IT 107-13-1, Acrylonitrile
(reaction with ketones)

RN 107-13-1 CAPLUS

CN 2-Propenenitrile (CA INDEX NAME)

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(CO2Et)(CH2)2CN, b0.1 121° n25D 1.4542, was prepd. in 37% yield by the method of Koelsch and Walker (C.A. 45, 1135f) and in poorer yield from III, iso-Pr2O, and BF3 by the method used by Hauser and Breslow (C.A. 34, 7875.6) to alkylate II. Other keto nitriles, AcCRR'CH2CH2CN, prepd. in a manner analogous to III: (R, R', yield (%), b.p. °C. (mm.), n25D resp., given): CH2CH2CO2Me, CO2Et, 100, 166° (1.7), 1.4510; CH2CH2CO2Et, CO2Et, 82, 168° (0.8), 1.4578; CH2Ph, CO2Me, 56, 163° (0.2), 1.5158; C6H13, CO2Et, 73, 157° (2.9), 1.4511; C7H15, CO2Et, 81, 145° (0.9), 1.4505; iso-Bu, CO2Et, 60, 125° (0.1), 1.4528. Also prepd. were CO.CH2.CH2.CH2.C(CO2Et)(CH2)2CN, 82, 145° (1.5), 1.4663; AcC(CH2CH2CN).CH2.C(CH2Cl).O.CO, 61, 199° (1.6), 1.4982; and BzCH(CO2Et)(CH2)2CN, 86, 176° (0.7), 1.5131. AcC(CH2OH)(CO2Et)(CH2)2CN, n25D 1.4585, was obtained in 94% yield from IV and formalin. Redn. of 93 g. AcC(CO2Et)(CH2CH2CO2Me)(CH2)2CN in 400 mL. EtOH by Raney Ni and H at 100° and 50 lb. pressure for 6 h., removal of the EtOH in vacuo, and filtration from dil. Et2O gave 36% 5-carbethoxy-9-methyl-2-oxo-1-azabicyclo[3.3.1]nonane, m. 170.4-1.3° (cor., from EtOH). The Et2O soln. gave 37.9 g. (43%) Et 3-(2-carbomethoxyethyl)-2-methylnipecotate, b1.4 139°, n25D 1.4740. A soln. of 115 g. Et 2-(2-cyanoethyl)cyclopentan-1-one-2-carboxylate in 400 mL. EtOH reduced by Raney Ni and H at 120° and 400 lb. pressure for 7 h. gave, on distn., 79 g. (73%) 4a-carbethoxyoctahydro-1-pyrindine (IX), b0.6 87°, n25D 1.4799 (cf. Henecka, Fr. 881,360), and 14.7 g. of a yellow oil, b0.4 153-209°, n25D 1.4852-8, m. 52.9-4.8° (cor., from Et2O), which may be the alc. obtained by redn. of the C:O bond. Redn. of 1 mol VI in 400 mL. MeOH by Raney Ni and H at 90° and 500 lb. pressure for 6 h. and treatment of the product with alc. HCl gave 62 g. 1-methyl-2-aza-8-oxaspiro[5.4]decan-7-one-HCl (X), m. 265-6.4° (cor., from EtOH). Hydrogenation of 116.2 g. Et 2-methylnipecotate in 400 mL. EtOH and 68 mL. 37% formalin at 25° and 400 lb. pressure with a buffered Pd-C catalyst required less than 45 min., giving on distn. 122.2 g. (98%) Et 1,2-dimethylnipecotate (XI), b0.2 73°, n25D 1.4557 [methiodide, m. 185.0-6.4° (cor.)]. The following piperidines (Xa) were prepd. in a similar fashion (R1, R2, R3, R4, % yield, b.p. °C. (mm.), n25D, resp.): H, Me, H, H, 85, 117° (760), 1.444; H, Me, H, CO2Et, 86, 59° (0.5), 1.4557 [1-PhNHCO deriv., m. 134.6-6.0° (cor.)]; Me, Me, H, CO2H, -, - (-), - [HCl salt, m. 185.8-8° (cor.)]; H, Me, Me, CO2Et, 89, 63° (0.1), 1.4581 [HCl salt, m. 164.4-5.0° (cor.)]; Me, Me, Me, CO2Et, 58, 67° (0.9), 1.4592; H, Me, iso-Pr, CO2Et, 84, 91° (0.3), 1.4666; Me, Me, iso-Pr, CO2Et, 82, 92° (0.6), 1.4642; H, Me, iso-Bu, CO2Et, 91, 98° (0.3), 1.4658; Me, Me, iso-Bu, CO2Et, 84, 95° (0.9), 1.4612; H, Me, C6H13, CO2Et, 85, 106° (0.2), 1.4627; Me, Me, C6H13, CO2Et, 80, 130° (1.9), 1.4609; H, Me, C7H15, CO2Et, 63, 120° (0.7), 1.4665; Me, Me, C7H15, CO2Et, 33, 136° (1.5), 1.4638; Me, Me, PhCH2, CO2Et, 81, 134° (0.2), 1.5110; H, Me, PhCH2, CO2Me, 78, 137° (0.6), 1.5335; Me, Me, PhCH2, CO2Me, 75, 132° (0.8), 1.5223; H, Me, Ph, CO2Et, 57, 131° (0.3), 1.5323; H, Me, -(CH2)2CO-, 30, - (-), - [HCl salt, m. 265-6°]; Me, Me, -(CH2)2CO-, 70, - (-), - [HCl salt, m. 72-5°]; Me, -(CH2)3-, CO2Et, 85, 83° (1.0), 1.4755; H, Me, (CH2)2CO2Et, CO2Et, 65, 133° (0.9), 1.4740; Me, Me, (CH2)2CO2Et, CO2Et, 86, 128° (1.0), 1.4726; H, Me, (CH2)3NH2, Me, 77, 80° (1.2), 1.5031 (b760 250-5°); di-HCl salt, m. 243-6°; monopicrate, m. 194-5°); H, Ph, H, H, 80, 80° (0.2), 1.5232 (readily hydrated on shaking with H2O); Me, Ph, H, CO2Et, 94, 116° (0.1), 1.5178. Redn. of 90 g. III in 400 mL. EtOH by Raney Ni and H at 60° and 600 lb. pressure for 1-3 h./mol H gave 89-93% 5-carbethoxy-6-methyltetrahydro-2-pyronimine, b0.9 103-6°, n25D

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ACCESSION NUMBER: 1950:22473 CAPLUS
DOCUMENT NUMBER: 44:22473
ORIGINAL REFERENCE NO.: 44:4426e-i,4427a-i,4428a-e
TITLE: Diene synthesis. XXII. The diene synthesis with aliphatic fulvenes
AUTHOR(S): Alder, Kurt; Ruhrmann, Rudolf
CORPORATE SOURCE: Univ. Cologne, Germany
SOURCE: Ann. (1950), 566, 1-27
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 44, 2479c, and Alder and Stein, C.A. 31, 7033.6. Adducts of dimethylfulvene (I) with maleic anhydride (II) can only be of the type (III). Past expts. indicate that addition at other points of I are excluded. The relative amts. of the "exo-A form" (IIIa), needles, m. 137° (from AcOEt) (cf. C.A. 24, 96) and the "endo-B form" (IIIb), rectangles, m. 112° (from AcOH), obtained vary, depending on the conditions of adduct formation. E.g., 5 g. I and 5 g. II in Et2O at 38° gave 3.3 g. IIIa and 2.6 g. IIIb; at 0°, 2.6 g. IIIa and 3.4 g. IIIb; in boiling C6H6, 6.2 g. IIIa and 0.7 g. IIIb. By heating in C6H6 IIIb is converted largely into IIIa. The corresponding acid (IVa) (from IIIa) m. 157° (decomposition) (from MeCN or AcOEt); IVb (from IIIb), m. 139° (decomposition). Heating IIIa with MeOH, gives the mono-Me ester of IVa, m. 124°, which with CH2N2 forms the di-Me ester (Va), m. 66° (from Et2O). With Busch-Stove's catalyst (C.A. 10, 2727) Va adds H, giving the corresponding dihydro derivative, m., 114° (from AcOEt). Va (2 g.) refluxed with 2 g. Na in 40 cc. MeOH, followed by addition of H2O, further refluxing, washing with Et2O, acidification, and extraction with AcOEt gave (in poor yield) the corresponding trans acid (VIa), m. 206°, (decomposition), complete hydrogenation of which with PtO2 gave the dihydro derivative (VIIa) of VIa, m. 205°, giving a sharp m.-p. depression when mixed with VIa. IIIa shake n 48 hrs. with 50% H2SO4 gave the cis lactone (VIIIa), m. 202° (from AcOEt); dihydro derivative (IXa) of VIIIa, m. 176°. Me ester (Xa) of VIIIa, m. 156° (from ligroin). The trans lactone (XIa), m. 171° (from AcOEt), was formed by treating Xa with MeONa; dihydro derivative of XIa, m. 176-8° (showing a sharp m.-p. depression when mixed with IXa). Xa adds PhN3, forming a compound (not analyzed), m. 209°, not identical with the (unanalyzed) hydrotriazole, m. 214° (obtained from PhN3 and IIIa), which in aqueous NaOH, followed by cooling and addition of AcOH, gave the phenyliminodicarboxylic acid (XII), m. 184° (from aqueous MeOH); di-Me ester of XII, m. 143° (from Et2O). In the above reaction if XII was not filtered but treated with AcOH until solution occurred, followed by addition of H2O and concentration in vacuo, there was formed a lactone monocarboxylic acid, m. 223° (from aqueous MeOH), whose mono-Me ester, C19H2104N, m. 227° (from MeOH). Partial reduction of IIIa with Pd-CaCO3 in AcOEt gave a dihydro derivative (XIII), C12H1403, m. 138° (from ligroin); corresponding free acid, m. 184° (from AcOEt), with loss of H2O; mono-Me ester, m. 138°; di-Me ester, m. 108° (from Et2O), yielding, with MeONa, a trans acid (XIIIa), m. 171°; this on hydrogenation gave VIIa, m. 205°. The mother liquors from VIIa probably contained another (impure) saturated acid (probably identical with XVI described below). XIII in aqueous Na2CO3 with 4% KMnO4, after extraction with H2O, filtration, and acidification of the filtrate, gave the alc. (XIV); Me ester, m. 150° (from ligroin-AcOEt). (In one such oxidation the reaction also gave small amts. of Me2CO.) XIII

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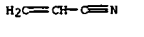
with 30% H2O2 in glacial AcOH and H2SO4 or with O3 in aq. NaOH gave, after extn. with Et2O and acidification, a compd. (XV), m. 252°; Me ester, m. 201° (from MeOH). The Na salt of XIII and NaOBr at 0°, followed by acidification, gave the Br analog of XV, m. 202° (from AcOEt); Me ester, C13H17O4Br, m. 141° (from MeOH). Further hydrogenation of XIII in AcOH with PtO2 gave an impure product, m. 101°, still showing unsatn. This, on oxidation with alk. KMnO4, conversion to the free acid, and treatment with AcCl, yielded the tetrahydro deriv. of IIIa, C12H16O3, m. 107-8° (from ligroin). The mono-Me ester of the corresponding dibasic acid, m. 112°, gave a di-Me ester (not isolated) which was converted with MeONa and hydrolysis into the trans acid (XVI), m. 208-9° (from AcOH) (giving a sharp m.-p. depression with VIIa). IIIb with PhN3 in AcOEt gave a hydrotriazole m. 203°, not identical with that obtained from IIIa. PtO2 and H acting on IIIb in AcOEt gave a dihydro deriv., C12H14O3 (XVII), m. 172°, adding MeOH to give the mono-Me ester (of the corresponding dibasic acid), m. 116° (from AcOEt), giving with CH2N2 a di-Me ester, m. 41° (from Et2O), which was converted into XIIIa, m. 172°. Ozonization of XVII in AcOH gave 80% of the theoretical yield of Me2CO. XVII with PtO2 and H gave 2 tetrahydro derivs., C12H16O3, of IIIb; a less sol. isomer, m. 107°, and a more sol. isomer, m. 80° (both from ligroin). These, on sapon. and hydrolysis gave the resp. cis acids (XVIII), m. 196°, and (XIX), m. 178°. XVIII was rearranged into the trans isomer, XVI. XIX on trans rearrangement gave VIIa. With (.tplbond.CCO2Me)2 under N, I gave the adduct C14H16O4, m. 101° (from MeOH), which with colloidal Pd in MeOH gave a dihydro deriv. (XX), m. 64-5° (from MeOH). Complete hydrogenation with PtO2 gave an unidentified oil. p-Benzoquinone and I in EtOH gave the adduct, C14H14O2, m. 118°. I and H2C : CHCN (after 6 weeks at room temp.) gave an (unanalyzed) adduct, m. 86-90°. Pentamethylenefulvene and II in Et2O at 0° (and subsequent standing at room temp.) gave the adduct "A" (XXI), C15H16O3, m. about 148° (depending on the rate of heating) (cf. Kohler and Kable, C.A. 29, 4334.7, who give 132°); the Et2O mother liquors from XXI gave on very slow evapn. the isomeric adduct B (XXII), m. 96° (from ligroin). The mother liquors from XXII were also carefully evapd. to dryness, treated with concd. aq. Na2CO3, and the resulting Na salt converted into the free acid (corresponding to XXII), C15H18O4, m. 137° (from ligroin). The over-all yield of XXI, XXII, and the acid was 74% of the theoretical. When heated in C6H6, XXII was recovered unchanged, whereas XXI was largely isomerized into XXII. XXI is the endo-adduct and XXII the exo-adduct. XXI added PhN3, giving the hydrotriazole, C21H21O3N3, m. 220° (from AcOEt) (decompn.). Hydrogenation with Busch-Stove catalyst gave a dihydro deriv. of XXI, m. 145°, yielding the dibasic cis-acid, m. 160° (decompn.) (from MeCN), the di-Me ester of which (not identified) was isomerized and hydrolyzed to the trans acid (XXIII), m. 229° (from AcOEt). XXII forms a hydrotriazole, C21H21O3N3, m. 191° (decompn.) (from AcOEt). When shaken with 50% H2SO4, XXII formed a lactone acid, C15H18O4, m. 204-5° (analogous to VIIIa); mono-Me ester, m. 112° (from petr. ether). The latter heated with PhN3 in AcOEt evolved N, yielding the Me ester of a phenylimino lactonic acid, C22H25O4N, m. 194°. The dihydro deriv. of XXII m. 106°; corresponding free acid (XXIV) m. 138° (decompn.), trans isomerization of which gave XXIII. XXIV adds HOBr at room temp. giving a bromo lactone acid, C15H19O4Br, leaflets, m. 167-8° (from aq. AcOH); mono-Me ester, C16H21O4Br, m. 133° (from MeOH).

IT 107-13-1, Acrylonitrile
(reaction with 6,6-dimethylfulvene)

L5 ANSWER 132 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)



L5 ANSWER 133 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1948:8243 CAPLUS
DOCUMENT NUMBER: 42:8243
ORIGINAL REFERENCE NO.: 42:1793e-h
TITLE: Mechanism of catalytic hydrogenation and dehydrogenation with rhodium
AUTHOR(S): Hernandez, L.; Nord, F. F.
CORPORATE SOURCE: Fordham Univ., New York, NY
SOURCE: Experientia (1947), 3, 489-490
CODEN: EXPEAM; ISSN: 0014-4754
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB A Rh catalyst prepared with polyvinyl alc. as a supporting colloid differs from similarly prepared Pd catalysts (cf. C.A. 35, 7810.7) in being sensitive to pH and to the presence of functional groups. E.g., the values of the reaction velocity constant, k + 106, are at room temperature 11.1, 10.8, 10.4, 10.1; 9.25, 9.02, 8.79, 6.25, and 1.85 for the hydrogenation of nitrobenzene parasubstituted with CN, CHO, NO2, COOH, I, Cl, Br, OCH3, and NH2 groups, resp., whereas the value for nitrobenzene is 8.33. Furthermore, for the Pd catalyst the value of k + 106 is 18.5 for nitrobenzene with or without the above list of p-substituted groups. For the hydrogenation of C:C in allylamine, acrylic acid, acrylonitrile, allyl alc., allyl acetate, allyl ethyl ether, and acrolein, the values of k + 105 for the Rh catalyst are 3.12, 2.63, 2.12, 2.08, 1.94, 0.97, and 0.28, resp. The authors conclude that Rh ionizes the H so that H+ is the effective hydrogenating agent, whereas for Pd, H atoms are involved. The authors also find that S enhances the activity of the Rh catalyst toward the dehydrogenation of formic acid and isopropyl alc. at 95°.

IT 107-13-1, Acrylonitrile
(hydrogenation on Rh, kinetics of)

RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)

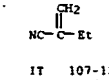
L5 ANSWER 134 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1947:9953 CAPLUS
DOCUMENT NUMBER: 41:9953
ORIGINAL REFERENCE NO.: 41:2074e-i
TITLE: Amino ethers
PATENT ASSIGNEE(S): Wingfoot Corp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 581994		19461031	GB	

AB Compds. having the formula NH2CH2C(X)HCH2OR, where X is Me, Et, or H, and R is an aliphatic group which may contain the ether, amino, and HO radicals, are obtainable by hydrogenating the nitriles resulting from the reaction between polyhydric alcs. and acrylonitrile (I), methacrylonitrile, or ethylacrylonitrile in the presence of alkaline catalysts. Thus O(CH2CH2OH)2 (II) 318, I 318, and NaOMe 2 g. gave 2,2'-bis(2-cyanoethoxy)diethyl ether, b8-14 227-38°, nD27 1.4478, d1528 1.067, which on reduction with H at 1000 lb./sq. in. in the presence of Raney Ni at 125-40° gave 2,2'-bis(3-aminopropoxy)-diethyl ether. With 1 mol. I and 1 mol. II, 2-(2-cyanoethoxy)-2'-hydroxydiethyl ether, b9 186°, nD22 1.4452, d1532 1.089, was obtained which gave 2-(3-aminopropoxy)-2'-hydroxydiethyl ether on hydrogenation. Glycerol (III) (1 mole) and 2 moles I give a mixture of 1,3-bis(2-cyanoethoxy)-2-hydroxypropane and 1,2-bis(2-cyanoethoxy)-3-hydroxypropane which hydrogenate to 1,3-bis(2-aminoethoxy)-2-hydroxypropane and 1,2-bis(2-aminoethoxy)-3-hydroxypropane. With 1 mole I and 1 mole III a mixture of 1,2-dihydroxy-3-(2-cyanoethoxy)propane and 1,3-dihydroxy-2-(2-cyanoethoxy)propane is formed which gives on reduction 1,2-dihydroxy-3-(3-aminopropoxy)propane and 1,3-dihydroxy-2-(3-aminopropoxy)propane. With 3 mols. I and 1 mole III 1,2,3-tris(2-cyanoethoxy)propane is formed, giving on hydrogenation 1,2,3-tris(3-aminopropoxy)propane, 1,3-bis(3-aminopropoxy)-2-hydroxypropane, 1,2-bis(3-aminopropoxy)-3-hydroxypropane, and PrNH2. With 2 moles I and 1 mole 2,3-butanediol (IV), 2,3-bis(2-cyanoethoxy)butane is obtained; with 1 mole of each, 1-hydroxy-3-(2-cyanoethoxy) butane and 1-(2-cyanoethoxy)-3-hydroxybutane are obtained. By hydrogenation , 2,3-bis(3-aminopropoxy)-, 2-(3-aminopropoxy)-3-hydroxy-, 1-hydroxy-3-(3-aminopropoxy)-, 1-(3-aminopropoxy)-3-hydroxy-, and 1,3-bis(3-aminopropoxy)butane are obtained. From 2-methyl-2,4-pentanediol and I, 2-methyl-2,4-bis(3-aminopropoxy)-, 2-methyl-2-(3-aminopropoxy)-4-hydroxy-, and 2-methyl-2-hydroxy-4-(3-aminopropoxy)pentane are obtainable. Cf. C.A. 39, 4624.1.

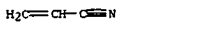
IT 1647-11-6, Butyronitrile, 2-methylene-
(and reaction products with polyhydric alcs., hydrogenation of)

RN 1647-11-6 CAPLUS
CN Butanenitrile, 2-methylene- (9CI) (CA INDEX NAME)



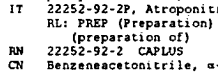
IT 107-13-1, Acrylonitrile
(reaction products with polyhydric alcs.,

L5 ANSWER 134 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
hydrogenation of)
RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)



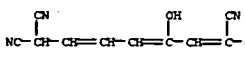
IT 126-98-7, Methacrylonitrile
(reactions of, with polyhydric alcs., hydrogenation of)
RN 126-98-7 CAPLUS
CN 2-Propenenitrile, 2-methyl- (CA INDEX NAME)

L5 ANSWER 135 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
between I and X, by adding 7 g. Ac2O to the reaction mixt. about 5 min. after the addn. of X. Alk. hydrolysis of XII yields phenylacetanilide, m. 118°. 5 g. PhCH2CHO in 20 cc. alc. reacts readily with 5 g. X, yielding N-phenylisophenylacetaldoxime, PhCH2CH:N(:O)Ph, m. 146°. Hydroxymethylenebenzyl cyanide (XIII) was prepd. as described by Walter and Schickler (J. Prakt. Chem. [2], 55, 31(1897)). K. found that the use of excess abs. alc. did not decrease the yield. Hydrogenation of XIII under 100-150 atm. H2 at 50-70°, with a supported Ni catalyst (Rupe, C. A. 13, 958) yields the aldime, which, on hydrolysis, yields I (Rupe, C. A. 21, 2559; 22, 771) if the hydrogenation is stopped after 5 hrs. If the hydrogenation is continued for 20 hrs. the basic fraction resulting from the hydrogenation yields, from 40 g. I 5.3 g. β- phenylpropylamine (Bz deriv., m.94°; cf. v. Braun, et al. (C. A. 7, 2567)); acid oxalate, m. 137°), b13 90°. A higher-boiling fraction, b13 180°, proved to be a secondary amine, and was assumed to be NH(CH2CHPhMe)2 on the basis of active H detns. and the analysis of the oxalate, m. 216°. 30 g. I, 15 g. anhyd. HCN and a trace of KCN were mixed and allowed to stand in the dark for 1 hr. in a flask provided with a CaCl2 tube and reflux condenser. If the mixt. was not liquid it was warmed slightly, then poured into ice water. The PhCH(CN)CH(OH)CN (XIV) so obtained m. 89°, when crystd. from C6H6 and dried, in vacuo at room temp. Traces of water during the recrystn. or heating during drying convert part of this dinitrile into a monoamide mononitrile of phenylmalic acid, m. 62°. Hydrolysis of 20 g. XIV with concd. HCl. gave 4.5 g. β-phenylmalic acid imide, m. 177°, which on warming with alkalies gave phenylacetic acid, m. 76°.
IT 22252-92-2P, Atroponitrile, β-hydroxy-
RL: PREP (Preparation)
(preparation of)
RN 22252-92-2 CAPLUS
CN Benzeneacetonitrile, α-(hydroxymethylene)- (9CI) (CA INDEX NAME)



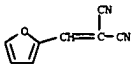
L5 ANSWER 135 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1937:44716 CAPLUS
DOCUMENT NUMBER: 31:44716
ORIGINAL REFERENCE NO.: 31:6214d-i,6215a-f
TITLE: Hydroxymethylene compounds
AUTHOR(S): Keller, Rudolf
SOURCE: Helvetica Chimica Acta (1937), 20, 436-50
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB The 1st step in the condensation of hydroxymethylenephenylacetaldehyde, PhC-(:CHOH)CHO (I) (cf. Rupe, C. A. 21, 2559; 22, 771), with NH2OH, aniline, PhCH2Cl and the 3 nitroanilines involves reaction of hydroxymethylene group, and subsequent reaction of the aldehyde group. In condensing with NH3, semicarbazide, hydantoin or urea, however, the 1st step in the reaction involves the aldehyde group. Ring formation (i. e., reaction at both groups) occurs in the reaction with PhNHNH2, NH2OH and o-C6H4(NH2)2. The condensations are effected by adding the substance directly, or in alc. solution, to I in 5-10 parts of alc. Anilinomethylenephenylacetaldehyde PhC(:CNHPh)CHO (II), m. 137°, is best prepared by using 10-20% excess I. The Schiff base PhC(:CHNHPh)CH:NPh (III), m. 130°, is obtained by using 2 mols. PhNH2 per mol. of I. Hydrolysis of III with excess 10% HCl yields II. Condensation of I with 2 mols. anthranilic acid (IV) yields the substance o-HO2CC6H4NHCH:CPhCH:NC6H4CO2H (V), m. 251°, soluble in hot AcOH and alkalies, insol. in alc., AcOEt, PhH, AcMe, petr. ether and CHCl3. Condensation of equimolar amts. of I and IV do not readily yield PhC(:CHNHC6H4CO2H)CHO (VI), even when excess I is used. VI, m. 220°, soluble in hot alc. pyridine, AcMe and AcOEt, is readily obtained, however, by acid hydrolysis of V. p-Carbethoxyphenylaminomethylenephenylacetaldehyde, p-EtO2CC6H4NHCH:CPhCHO, m. 131°, soluble in most organic solvents, is obtained by equimol. condensation of I and p-EtO2CC6H4NH2 (VI). If 2 mols. VI are employed there results PhC(:CHNHC6H4CO2Et)CH:NC6H4CO2Et m. 145°. Condensation of equimol. amts. of α-C10H7NH2, (VII) with I yields a mixture of α-naphthylaminomethylene-phenylacetaldehyde (VIII), m. 82°, readily soluble in alc. PhH, CHCl3, AcOEt, ether and AcMe, and PhC(:CH-NHC10H7)CH:NC10H7 m. 233°, slightly soluble in alc., which is also obtained by the condensation of 2 mols VII with I. A semicarbazone of VIII cannot be obtained, nor will VIII react with a 2nd mol. of VII. Only 1 mol. of β-C10H7NH2 reacts with I, yielding β-naphthylaminomethylenephenyl-acetaldehyde, m. 233°. Regardless of the proportions of p-MeC6H4NH2 and I employed, the only product obtained is p-toluidinomethylenephenylacetaldehyde, m. 152°, although the Schiff base PhC(:CHNHC6H4Me)CH:-NHC6H4Me, m. 129°, is obtained from o-MeC6H4NH2. I condenses with 2 mols α-aminocamphor, giving phC(:CHNHCH.Co.C8H14)CH:NCH.CO.C8H14 (IX), m. 156°, in 50% yield. IX forms a perchlorate, HCl salt and sulfate. A study of the rotation dispersion of benzene solns. of IX shows that the rotation reaches a maximum value of -54.4 at 5460 A. I condensed with PhNHCONHNH2 yields a phenylcarbazidomethylenephenylcarbazone, PhC(:CHNHNHCONHPh) CH:NNHCONHPh, m. 216°. 3 g. I in 15 cc. HCO2H or AcOH condensed with 2 g. PhNHOH (X), added in small portions to the stirred, cooled solution, yields 10% of the diphenylisoxazolone, PhC:CH.NPh.O.C:O (XI) m. 167°, insol. in ether, PhH, AcOEt, AcMe and AcOH, soluble in alc., CHCl3 and C5H5N. XI is hydrolyzed by EtOH-KOH (10%) to trans-phenylhydroxylaminomethylenephenylacetic acid, m. 132°. Acetoxymethylenephenylacetanilide, PhC(:CHOCOCH3) CONHPh (XII), m. 141-2°, can also be obtained in 10-20% yield by the reaction

L5 ANSWER 136 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1936:50515 CAPLUS
DOCUMENT NUMBER: 30:50515
ORIGINAL REFERENCE NO.: 30:6751h-i,6752a-e
TITLE: New dyestuffs from furfural
AUTHOR(S): Boehm, Theodor; Grohnwald, Magda
SOURCE: Arch. Pharm. (1936), 274, 318-26
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB The peculiar reaction, first noted by Heuck (Ber. 28, 2253(1895)), leading to the formation of a dyestuff from furfuralmalonitrile and NH3 or KOH, has been subjected to renewed study with the following result: The dyestuff has the constitution (CN)2CHCH:CHCH:C(OH) CH:C(CN)2 (I) and appears only in the presence of bases, which operate in the nature of catalysts in that they constitute apart of the intermediate product, as shown in benzylamine as the base, in which case glistening crystals having the composition C15H13ON3 (II) are obtained from equimol. proportions of C4H3O.CHO, CH2(CN)2 and PhCH2NH2. With HCl II yields the salt C15H13ON3.HCl, and with PhN2H3 the compound C14H12ON4, in which the PhCH2NH2 has been replaced by the hydrazine. On the addition of CH2(CN)2 to II in alc., the dyestuff I is instantly formed, with separation of PhCH2NH2, from which it follows that the furan ring no longer exits in II, in other words the amine exercises the function of splitting the furan ring in furfuralmalonitrile. A product fully analogous in structure to I is formed by substituting CNCH2CONH2 for malonitrile, thus: H2NOC(NC)CHCH:CHCH:C(OH)CH:C(CN)CONH2 (III). Finally, on treating I with concentrated HCl, a product was obtained having the composition C11H8O2N4 (= I + H2O), and crystallizing in dark blue crystals. The investigation was rendered very difficult owing to the tendency of the dystuffs to retain varying amts. of the solvent (EtOH, AcOH), which on drying was obstinately held by the crystals. Furfuralmalonitrile was prepared in almost quant. yield by mixing freshly distilled furfural (9.6) with CH2(CN)2 (6.6) in 5 cc. alc., followed by the addition of 2 drops PhCH2NH2, and washing the crystallized mass with ice-cold EtOH to a faint rose color. 6-Benzyl-amino-1,3,5-hexatrien-3-ol-1,1-dinitrile, blue glistening rods m. 161° (HCl salt, reddish yellow, with 1 mol. alc. m. 140°). The corresponding PhN2H3 derivative, golden yellow needles, m. 186°. The dyestuff I, blue-violet needles from MeOH, m. 225° (decomposition), and from EtOH blue violet felty needles m. 225° (decomposition) (Ac derivative brilliant orange, m. 210°); hydrogenation of I (+2H) yielded the yellow product, C13H12O2N4, m. 94-6°; saponification of I with concentrated HCl gave a product, black-blue prisms (from EtOH), m. 250-5°, which on drying in vacuo at 140° became amorphous and dark red; finally recrystd. from a mixture of AcOH and Ac2O it gave the dark blue substance, C11H8OZN4, probably an acid amide (Ac derivative, yellow, m. 215-20°). The dyestuff III, dark red, m. 245° (decomposition).
IT 859772-09-1, 1,3,5-Heptatriene-1,1,7,7-tetranitrile, 3-hydroxy-
(and derivs.)
RN 859772-09-1 CAPLUS
CN 1,3,5-Heptatriene-1,1,7,7-tetranitrile, 3-hydroxy- (3CI) (CA INDEX NAME)

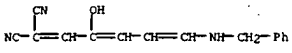


IT 3237-22-7P, Malononitrile, 2-fural- 859195-83-8P, Malononitrile, (5-benzylamino-2-hydroxy-2,4-pentadienylidene)-, -HCl 859195-90-7P, Malononitrile, (5-benzylamino-2-hydroxy-2,4-pentadienylidene)- 859199-90-9P, Malononitrile, (2-hydroxy-5-β-phenylhydrazino-2,4-pentadienylidene)- 859772-13-7P, 1,3,5-Heptatriene-1,7-dicarboxamide, 1,7-dicyano-3-hydroxy-
RL: PREP (Preparation)
(preparation of)

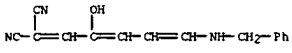
RN 3237-22-7 CAPLUS
CN Propanedinitrile, 2-(2-furanylmethylene)- (CA INDEX NAME)



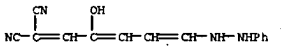
RN 859195-83-8 CAPLUS
CN INDEX NAME NOT YET ASSIGNED



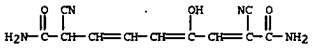
RN 859195-90-7 CAPLUS
CN INDEX NAME NOT YET ASSIGNED



RN 859199-90-9 CAPLUS
CN INDEX NAME NOT YET ASSIGNED



RN 859772-13-7 CAPLUS
CN 1,3,5-Heptatriene-1,7-dicarboxamide, 1,7-dicyano-3-hydroxy- (3CI) (CA INDEX NAME)



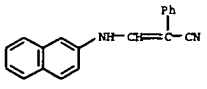
ACCESSION NUMBER: 1936:50396 CAPLUS
DOCUMENT NUMBER: 30:50396
ORIGINAL REFERENCE NO.: 30:6704c-i,6705a-e
TITLE: Unsaturated acids from hydroxymethylene compounds
AUTHOR(S): Borsche, W.; Niemann, J.; Hartmann, H.
SOURCE: Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B: Abhandlungen (1936), 69B, 1993-8
CODEN: BDCBAD; ISSN: 0365-9488
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB Phalnikar and Nargund (C. A. 30, 5186.6) have recently published a "new process for the synthesis of α-substituted glutaconic acids," in which is described the preparation of such acids by the condensation of hydroxymethylenepropionic (I), -hydrocinnamic (II) and -phenylacetic ester (III) with malonic ester and pyridine. The authors of the present paper report expts. of a similar nature; they carried out some 5 yrs. ago, not only with the above esters but also with the hydroxymethylene derivs. of PhCH2CN, PhCOMe, PhCOEt, desoxybenzoin, cyclohexanone and camphor and with formylfluorene, and also with NCCH2CO2Et in addition to malonic ester. Of the hydroxymethylene derivs., only those of the esters and camphor and formylfluorene gave unsatd. acids. The PhCOEt and cyclohexanone derivs. were in large part recovered unchanged; that of desoxybenzoin was apparently mostly cleaved with regeneration of desoxybenzoin. The less smooth reaction of the PhCH2CN derivative has not yet been definitely cleared up. The assumption of P. and N. that the hydroxymethylene esters react in the aldehyde form does not seem necessary; the authors believe that the 1st product of the condensation, e. g., MeCH(CO2R)CH(OH)CH(OH)CH(CO2H)2, is formed by addition of malonic ester to the hydroxymethylene form, for even where the yields of unsatd. acid were exceptionally good no aldehyde could be detected by means of the Dobner cinchoninic acid synthesis. PhCH2CHO heated with malonic ester and pyridine gives chiefly PhCH:CHCH2CO2H, along with a little PhCH2CH:CHCO2H; hence, the condensation products of III with malonic and cyanoacetic esters are probably 4-phenyl-4-carbethoxy-Δ3-butenoic acid (IV) and Et 2-phenyl-4-cyano-Δ2-butenoate (V), resp. The free acid (VI) of IV is quite smoothly decarboxylated, on distillation, to PhCH:CHCH2CO2H, and that of V on heating with NaOH surprisingly gives PhCH:CHCH2CN, m. 61-2°. The acid obtained from formylfluorene and malonic ester is likewise probably β-(9-fluorenylidene)propionic acid (VII). On the other hand, there has as yet been obtained no indication that in the condensation of I with malonic ester the double bond is shifted away from the carboxyl group; the product (VIII) may therefore well be MeCH(CO2R)CH:CHCO2H. The greatest difficulty seems to be to derive a formula for the crystalline unsatd. acid C13H18O3 (IX) obtained, along with an oil, from hydroxymethylenecamphor. Rupe and Burckhardt (C. A. 11, 2671) obtained the Et ester of this acid from "chloromethylenecamphor" and AcCHNaCO2Et in alc. and assigned to the acid the structure of a β-(3-camphorylidene)propionic acid (X). The ease with which it splits off CO2 and its conversion into the doubly unsatd. lactone C13H16O2 (XI), b18 187°, m. 62-3°, by solution in concentrated H2SO4 would indicate, however, that it is an α,β-unsatd. acid. R. and B, therefore assume that under the influence of the H2SO4 water adds at the double bond of IX. The present authors, however, have obtained X under conditions excluding such addition of water, i. e., by treating IX with SOCl2. IX may exist in 2 forms in a kind of "allyl tautomerism." The oily part of the product from hydroxymethylenecamphor and malonic ester gave with SOCl2, along with XI, a substance, b13 117-19°, having

the compn. C13H17O2Cl of the expected chloride. Whether it is such and whether it corresponds to the trans-form of the α,β-unsatd. acid showing no tendency to form a lactone or to 1 of the 2 stereoisomeric camphorylidenepropionic acids remains to be detd. From 13 g. I with malonic ester is obtained 6.7 g. trans-α-methylglutaconic acid, m. 144°; with NCCH2CO2Et, Et 2-methyl-4-cyanobutenoate, b15 135-7°. VI, m. 166-7°; di-Me ester, from VI and boiling MeOH-H2SO4, b15 180-2°, hydrogenated in MeOH with a Pt catalyst to di-Me α-phenylglutarate, b13 178-9° (anhydride, from the free acid heated in vacuo, m. 93°). V, b19 183-7°. Et 2-phenyl-4-cyanobutenoate, from V by catalytic hydrogenation, is readily sapond. to the acid, m. 132°. IX, m. 104-6°; Me ester, b18 180-1°. 3-Ethylidenecamphor, from IX distd. under atm. pressure, b764, 224-6°. Camphorylidenepropionitrile, from hydroxymethylenecamphor and NCCH2CO2Et (yield, about 80%), m. 72°, b16 188-92°. VII, m. 202-3°, was obtained in about 2.6 g. yield from 19.4 g. α-formylfluorene, together with about 17.5 g. unreacted formylfluorene, b13 198-200°, whose dark yellow dinitrophenylhydrazone m. 208° (decompn.). In attempts to use the hydroxymethylene derivs. of PhCH2CO2Et, PhCH2CN and camphor for Dobner cinchoninic acid syntheses there was obtained in all cases with β-C10H7NH2 2-methyl-5,6-benzocinchoninic acid; the PhCH2CN and camphor derivs. gave, in addn., the "enamines" PhC(CN):CHNHC10H7, yellow, m. 190-1°, and (C10H14O):CHNHC10H7, yellowish, m. 186-7°.

IT 106885-61-4P, Atroponitrile, β-(2-naphthylamino)-
RL: PREP (Preparation)
(preparation of)

RN 106885-61-4 CAPLUS
CN Atroponitrile, β-(2-naphthylamino)- (7CI) (CA INDEX NAME)



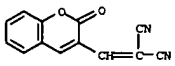
L5 ANSWER 138 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1934:8303 CAPLUS
DOCUMENT NUMBER: 28:8303
ORIGINAL REFERENCE NO.: 28:1033b-i,1034a-g
TITLE: The coumarin group. II. Synthesis of certain coumarinaldehydes; the catalytic hydrogenation of acid chlorides
AUTHOR(S): Boehm, Theodor; Schumann, G.
SOURCE: Arch. Pharm. (1933), 271, 490-513
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C. A. 25, 2145. The odorous and non-odorous properties of the various coumarin derivs. are discussed from the standpoint of their chemical composition
Of the 6 possible coumarinaldehydes, only 1 was heretofore known. Accordingly, the question arose whether and to what extent the relative position of the CHO group affected the aroma. Attempts to prepare the unknown isomeric aldehydes, for the present notably the synthesis of coumarin-3-aldehydes, are described. In addition thereto and for purposes of
comparison, umbelliferone-3-aldehyde (IV) and coumarin-3-acrylaldehyde (VII) were also prepared The general procedure followed was that of Rosenmund and the initial materials employed were the corresponding carboxylic acids, whose acid chlorides were reduced catalytically in presence of Pd. With respect to the physiol. properties of the new aldehydes, coumarin-3-aldehyde (I) no longer possesses the typical odor of coumarin, but has on the other hand the property of irritating the mucosa of the nose and throat. Since both odorous and irritant effects are not unrelated factors, it follows that the osmophoric aldehyde group in the osmophoric lactone ring of coumarin effects an increase in strength or potency of the coumarin itself. Reference is made to a similar phenomenon in the case of PhCH:CH-CHO (II) and PhC: CCHO (III), wherein the double bond of the side chain of the former becomes a triple bond in the latter; while the odor of III is still reminiscent of II, it is no longer pleasant, but on the contrary irritating. This effect is obviously, as with coumarinaldehyde, due to superimposition of the osmophoric groups. In contrast to coumarinaldehyde IV behaves rather indifferently, merely emitting on heating a weak phanol-like odor. I and IV are therefore opposed to one another like coumarin and umbelliferone. No regularity exists, however, in this analogy. This is apparent in the following example: Et coumarincarbcxylate (V) is odorless, while the corresponding umbelliferone ester (VI) smells strongly of coumarin, a marked reversion of the relationship previously noted. Worthy of note too is the fact that IV still remains indifferent when the phenolic HO is replaced by AcO or the OCO2Me group. Normally, VII is odorless, but on heating to the in. p. emits a weak coumarin-like odor. Substitution of the osmophoric NO2 group for the CHO radical effects no change therein. This NO2 derivative, coumarin-3-α-nitroethylene (VIII), was obtained by condensation of I with nitromethane. I also reacts in a normal manner with CH2(CN)2, CH2(CO2H)2, CNCH2CONH2 and CNCH2COCH2CO2Et. Contrary to expectation, all these condensation products were odorless. An abnormal result was observed in the condensation with CH3COCH2CO2Et, the reaction being carried out in alc. in the presence of C5H11N. In this instance a well-defined crystalline product of the composition (C7H8O2)n was formed, the
constitution of which is as yet unexplained. The condensation with CH2(COEt)2 was equally irregular, in that the substance obtained had the constitution IX. Only after treatments with Ac2O and consequent splitting off of H2O did it yield the unsatd. compound (X), which should have been the immediate product of condensation. IX merits especial interest, since, if

L5 ANSWER 138 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
the formula given is correct, which there is no reason to doubt, here for the first time no unsatd. compd., but instead a β-HO compd. results from a Knoevenagel condensation. This is insofar of importance since the character of the Knoevenagel reaction has in spite of all attempts to clarify it remained more or less a mystery. A broader basis has thus been created for the future treatment of the problem. The results of the first attempts to prep. I were unfavorable. Only after numerous expts. had shown that a partial poisoning of the catalyst by introduction of certain foreign material via Rosenmund and co-workers did not necessarily lead to satisfactory yields of aldehydes, more attention was directed, and with success, to the temp. (relatively low) prevailing in the soln. (xylene) during the catalytic reduction. Coumarincarboxylyl chloride, C10H5O3Cl, obtained from the corresponding acid with CSCl2, m. 147-8° yielded on reduction I, m. 131-2° (p-nitrophenylhydrazone, C16H11O4N3, yellow, m. 287-8° (decompn.); semicarbazone, yellow, m. 265-6° (decompn.); oxime, m. 207° (decompn.)). [With H. H. Hansen.] Coumarin-3-acrylic acid, m. 266° (Et ester, yellow, m. 122°; acid chloride, yellow, m. 197-8°); the acid yielding on reduction VII, faintly yellow, m. 155-6° (p-nitrophenylhydrazone, m. 289-90° (decompn.); oxime, m. 207°; semicarbazone, m. 242°). VIII, m. 143-4°. IX, yellowish needles with 1 mol. H2O of crystn., m. 207°. I condensed with CH2(CO2H)2 gave coumarin-3-methylene-malonic acid, C13H8O6.H2O, yellow, m. 207°. I with CH2(CO2Et)2 gave IX, m. 117° which with Ac2O gave X, brilliant leaflets, m. 93-5°. Condensation of I with AcCH2CO2Et yielded the product (C7H8O2)n, m. 81-2°. With CH2(CN)2, I gave coumarin-3-methylenemalonic dinitrile, yellow, m. 198° (decompn.). Among other condensation products characterized are: coumarin-3-[α-cyanoacrylic amide], C13H8O3N2, yellow, m. 233°; Et coumarin-3-αcyanoacrylate, yellow, m. 202°; condensation product, C17H21O5N, from resorcinol aldehyde, CH2(CO2Et)2 and C5H11N, m. 152-4°, yields with Na2CO3 soln. the strong odor of C5H11N, and on addn. of HCl the Et umbelliferone-3-carboxylate, m. 171°, previously described by Pechmann and Graeger (Ac deriv., C14H12O6, m. 153-4°, in neutral alc. soln. fluoresces faintly blue; the corresponding acid, C12H8O6, m. 210-11°, is likewise faintly fluorescent in aq.-alc. soln., and the chloride, m. 189-90° the latter on reduction giving the aldehyde, faintly yellow, m. 165-6°, faintly bluish green fluorescent (p-nitrophenylhydrazone, m. 280° (decompn.)). Carbomethoxyumbelliferone-3-carboxylic acid, C12H8O7, m. 214-15°. The corresponding carbethoxy deriv., m. 167° (acid chloride, m. 144-5°; aldehyde, m. 134-5°, fluoresces strongly bluish green (p-nitrophenylhydrazone, m. 263-5°)). IV forms yellow prisms carbonizing above 300° (p-nitrophenylhydrazone, red, carbonizes above 300°; oxime, yellow, m. 224-5°). Et daphnetin-3-carboxylate, C12H10O6, yellow, m. 231-2° (di-Ac deriv., m. 129-30°); free acid, yellow, m. 263° (di-Acderiv., m. 213-14°).

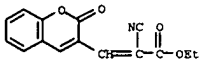
IT 859195-76-9P, Malononitrile, (2-keto-1,2-benzopyran-3-ylmethylene-) 860564-78-9P, 1,2-Benzopyran-3-acrylic acid, α-cyano-2-keto-, ethyl ester 860564-82-5P, 1,2-Benzopyran-3-acrylamide, α-cyano-2-keto-
RL: PREP (Preparation)
(preparation of)

RN 859195-76-9 CAPLUS
CN INDEX NAME NOT YET ASSIGNED

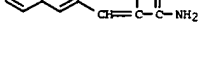
L5 ANSWER 138 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)



RN 860564-78-9 CAPLUS
CN 1,2-Benzopyran-3-acrylic acid, α-cyano-2-keto-, ethyl ester (3CI) (CA INDEX NAME)



RN 860564-82-5 CAPLUS
CN 1,2-Benzopyran-3-acrylamide, α-cyano-2-keto- (3CI) (CA INDEX NAME)



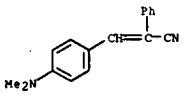
L5 ANSWER 139 OF 139 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1932:20813 CAPLUS
DOCUMENT NUMBER: 26:20813
ORIGINAL REFERENCE NO.: 26:2185c-i,2186a-b
TITLE: p-Dimethylaminobenzal ketones. II. Auxochromic groups
AUTHOR(S): Rupe, H.; Collin, August; Sigg, Walter
SOURCE: Helvetica Chimica Acta (1931), 14, 1355-69
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB These investigations indicate that the NMe2 group acts strongly to deepen color in unsatd. ketones, especially in mols. having the group -CO.CH:CH-. The diphenylhexatriene of Kuhn and Winterstein (C. A. 22, 1767) is yellow while 1-phenyl-7-(p-dimethylaminophenyl)-1,3,6- heptatrien-5-one (I) is red and their diphenyloctatetraene is greenish chrome-yellow while 1-phenyl-9-(p-dimethylaminophenyl)-1,3,5,8-nonatetraen-7-one (II) is vermilion. α-Phenyl-p-dimethylaminocinnamonitrile, Me2NC6H4CH:C(CN)Ph (III), obtained by the method of Kauffmann (C. A. 11, 2805), intensely yellow with bright yellowish green fluorescence, m. 136°; HCl salt, white, m. 184-8° (decomposition); acid sulfate; perchlorate, decomps. 164-70°; methiodide, m. 185°; methosulfate, C19H22O4N2S, m. 261°; 60% H2SO4 hydrolyzes the nitrile to the corresponding acid, yellowish brown needles, m. 223°. (Me2NC6H4CH2CHPhCH2)2NH (IV), obtained in 6 g. yield from 40 g. III by hydrogenation in 500 cc. EtOH and AcOH mixture with 40 g. Ni catalyst at 100 atms. and 40-50°, m. 107°; picrolonate, brownish yellow prisms, m. 207°. Another secondary amine isomeric with IV, possibly the meso-form, is obtained in 4 g. yield from the reaction producing IV, m. 85° (mixed m. p. with IV, 92-6°); phenylthiourea derivative, m. 166°. The primary amine Me2NC6H4CH2CHPhCH2NH2 is obtained in 9 g. yield from the reaction which produces IV, yellow oil, b13 225-9°, which on standing forms a nearly colorless crystal cake; phenylthiourea derivative, m.
147°; picrolonate, citron-yellow, m. 222°.
p-Dimethylaminobenzaldesoxybenzoin ketimide, Me2NC6H4CH:CPh:NH (V), obtained by adding 10 g. III to 31 g. PhBr and 5 g. Mg in C6H6, warming 4 hrs. on the water bath and extracting with ether after adding water, bright yellow, m. 150°, dissolves in dilute acids with blood-red color, dyes mordanted cotton red and unmordanted cotton dirty yellow. Hydrolysis of V with 20% boiling HCl for 0.5 hr. yields p-dimethylaminobenzaldesoxybenzoin. yellow, m. 167°, soluble in HCl without color and identical with the compound of Kauffmann (C. A. 11, 2794). Et α-cyano-p-dimethylaminocinnamate (VI), obtained by warming equivalent amts. of Me2NC6H4CHO and NCCH2CO2Et in alc. with NaOH, orange-yellow, m. 122°; perchlorate, pale yellow; methosulfate, pale yellow m. 197°. Me2SO4 also forms an addition product with Me2NC6H4CH:CHCOMe, m. 202°, easily hydrogenated.
α-Cyano-p-dimethylaminocinnamic acid, obtained by warming VI on the water bath with 30% NaOH until the orange color becomes pale yellow, orange- red, m. 212°. Longer treatment of VI with NaOH gives Me2NC6H4CHO. α-Dimethylaminobenzyl-β-aminopropionic acid, obtained by hydrogenating at 80 atms. and 40-50° for 5 hrs. 20 g. VI in 250 cc. alc., 250 cc. AcOH and 50 cc. water with 60 g. Ni catalyst, and hydrolyzing the yellow oil formed with HCl, m. 235°; the Cu salt was prepared and analyzed; 2 g. dissolved in water and heated to dryness with 2 g. KCNO and then to dryness with 20% HCl and taken up with water gave a white precipitate with NaOH,
crystallizing from alc., m. 237°, of 5-dimethylaminobenzylhydrouracil. I was obtained by warming 40 g.

Me2NC6H4CH:CHCOMe in 300 cc. alc. with 20 g. PhCH:CHCHO and NaOH at 40°, intensely red, m. 150°; HCl salt, green and unstable; methiodide, paleocher-colored crystals from MeOH, m. 175°. Phenylbutyl p-(dimethylaminophenyl)- ethyl ketone, obtained in 25 min. by hydrogenating 20 g. I in 250 cc. alc., 250 cc. AcOEt and 50 cc. water with 20 g. Ni catalyst and the theoretical vol. of H for the 3 double bonds (4.75 l.), purifying the yellow oil formed after removal of solvents by crystn. of the semicarbazone, and recovering the ketone by warming with oxalic acid, b0.05 172-5°, pale yellow oil becoming red on standing, forms a colorless soln. in HCl; semicarbazone, m. 105°. II was obtained by warming 20 g. Me2NC6H4CH: CHCOMe in 150 cc. alc. with 17 g. of the phenylpentadienal of Vorl.acte.ander (C. A. 23, 3687) and NaOH, vermilion, m. 184°. Phenylhexyl p-(dimethylaminophenyl)ethyl ketone, obtained by hydrogenating 20 g. II in 500 cc. alc. and 50 cc. water with 20 g. Ni catalyst and 5.85 l. H at 60°, and purifying the yellow oil by crystn. of the oxalate from alc. since the semicarbazone did not form, pale yellow oil, b0.1 187°, setting to a colorless crystal mass, m. 27-8°; oxalate, m. 105°.

IT 1222-61-3, Acrylonitrile, β-(p-dimethylaminophenyl)-α-phenyl-
(and derivs.)

RN 1222-61-3 CAPLUS

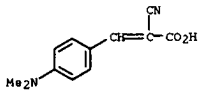
CN Benzeneacetonitrile, α-[[4-(dimethylamino)phenyl]methylene]- (9CI) (CA INDEX NAME)



IT 57711-73-6P, Cinnamic acid, α-cyano-p-dimethylamino-
860737-69-5P, Ammonium, [p-(β-carboxy-β-cyanovinyl)phenyl]trimethyl-, methylsulfate
RL: PREP (Preparation)
(preparation of)

RN 57711-73-6 CAPLUS

CN 2-Propenoic acid, 2-cyano-3-[4-(dimethylamino)phenyl]- (9CI) (CA INDEX NAME)



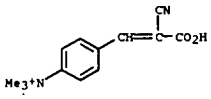
RN 860737-69-5 CAPLUS

CN Ammonium, [p-(β-carboxy-β-cyanovinyl)phenyl]trimethyl-, methylsulfate (3CI) (CA INDEX NAME)

CM 1

CRN 860737-68-4

CMF C13 H15 N2 O2



CM 2

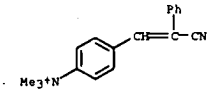
CRN 21228-90-0

CMF C H3 O4 S

IT 802333-08-0, Ammonium, [p-(β-cyanostyryl)phenyl]trimethyl-
(salts)

RN 802333-08-0 CAPLUS

CN Ammonium, [p-(β-cyanostyryl)phenyl]trimethyl- (8CI) (CA INDEX NAME)



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MISSING TERM AFTER YLONITRIL?>
Operators must be followed by a search term, L-number, or query name.

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        113616 ?ACRYLONITRIL?
L6          79 L5 AND ?ACRYLONITRIL?

=> d l6 70-79 ibib abs hitstr
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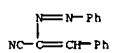
L6 ANSWER 70 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1957:71509 CAPLUS
DOCUMENT NUMBER: 51:71509
ORIGINAL REFERENCE NO.: 51:12929h-i,12930a-i,12931a-c
TITLE: Reduction of some α-phenylhydrazono ketones with alkali borohydrides
AUTHOR(S): Bowman, R. E.; Franklin, C. S.
CORPORATE SOURCE: Parke, Davis & Co., Ltd., Hounslow, UK
SOURCE: Journal of the Chemical Society (1957) 1583-8
CODEN: JCSOA9; ISSN: 0368-1769
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 51:71509

AB Several α-phenylhydrazono ketones (I) were reduced by alkali borohydrides to the corresponding alcs. (II) although in a few cases these proved too unstable for isolation. Some reactions of the alcs. were examined, including hydrogenolysis as exemplified by the reduction of Et β-hydroxy-α-phenylhydrazonobutyrate (IIa) to an equimolar mixture of racemic (III) and allothreonine (IIIa). I were reduced by the following 3 methods: (A) a 1% solution of NaBH4 or KBH4 (0.5 mole) in aqueous alc. was added dropwise to 1 mole I in alc., and after 1-2 hrs. at 20-40° the mixture concentrated in vacuo, II isolated by extraction with EtOAc, and crystallized from C6H6-ligroine, except where otherwise stated; (B) a similar procedure but the temperature was kept below 25°, and the solution acidified with 2N H2SO4, and after removal of the inorg. salts, the product isolated as before; (C) reduction as in B but under N and with an equimolar amount of 10% KBH4 in H2O and on concentration the product solidified and crystallized The following were thus obtained (method indicated in parentheses): pyruvaldehyde gave 53% lactaldehyde phenylhydrazone, m. 90.5-1.5° (A); phenylglyoxylaldehyde phenylhydrazone gave mandelaldehyde phenylhydrazone, needles, m. 103° (A); 3-phenylhydrazonopentane-2,4-dione gave 40% 4-oxo-3-phenylhydrazonopentan-2-ol, yellow needles, m. 138-8.5° (A); Et β-oxo-α-phenylhydrazonobutyrate gave 55% IIa, prisms, m. 93-4° (B); β-oxo-β-phenyl-α-phenylhydrazonopropionitrile gave 11% β-phenyl-α-phenylazoacrylonitrile, orange needles, m. 119-20° (B); 2-nitro-1-phenyl-2-phenylhydrazonoethanol (IIb) (from the corresponding nitro ketone) in 67% yield as orange needles, m. 121-2° (from xylene) (B); 2-oxo-2-phenyl-1-phenylhydrazonoethanesulfonic acid gave 13% mandelic acid phenylhydrazide, needles, m. 181-3° (from alc.) (B); Et α-oxo-β-phenylhydrazonosuccinate gave 77% IIb, needles, m. 163° (from EtOAc) (C) (acetate, prisms, m. 74-5°); Et α-oxo-β-p-nitrophenylhydrazonosuccinate gave 50% 3-ethoxycarbonyl-4-hydroxy-1-p-nitrophenylpyrazol-5-one (IIIb), prisms, m. 198° (decomposition) (from alc.) (C); Et β-cyano-α-oxo-β-phenylhydrazonopropionate gave 57% 3-cyano-4-hydroxy-1-phenylpyrazol-5-one, needles, m. 157° (decomposition) (from MeNO2) (C); Et α,γ,-dioxo-β-phenyl-hydrazonovalerate gave 26% 4-hydroxy-3-(1-hydroxyethyl)-1-phenylpyrazol-5-one, prisms, m. 161° (decomposition) (from alc.) (C). IIb (50 g.), 28.4 g. MeI, and 50 ml. MeOH heated 16 hrs. at 105° in an autoclave gave 37 g. 3-ethoxy-carbonyl-4-hydroxy-2-methyl-1-phenylpyrazol-5-one (IV), needles, m. 164°; acetate, m. 71-2°; benzoate, needles, m. 115-16° (from C6H6-ligroine); diphenylacetate, plates, m. 120-1°; p-nitrobenzoate, prisms, m. 151°; p-aminobenzoate, yellow needles, m. 186° (from alc.). IV (2 g.) in 35 ml. alc. treated overnight with 2 moles 2N NaOH gave 1.8 g.

L6 ANSWER 70 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
3-carboxy-4-hydroxy-2-methyl-1-phenylpyrazol-5-one (V), needles, m. 134° (decompn.). V heated to 200° until evolution of CO2 ceased gave 4-hydroxy-2-methyl-1-phenylpyrazol-5-one (VI), needles, m. 191-2° (from PhMe), pKa' 9.3 in 50% MeOH. IV (1 g.) in 10 ml. dioxane added to a suspension of anilinomagnesium iodide (2 moles) in Et2O gave 0.3 g. 4-hydroxy-2-methyl-1-phenyl-3-(N-phenylcarbamoyl)pyrazol-5-one (VII), needles, m. 231-2° (decompn.) (from aq. alc.). PhCH2Cl (12.7 g.) and 13 g. IV in 1 l. EtCOMe refluxed 16 hrs. with 27 g. K2CO3 gave 16.5 g. 4-benzyloxy-3-ethoxycarbonyl-2-methyl-1-phenylpyrazol-5-one (VIII), m. 84-5° (from ligroine). Hydrolysis of VIII yielded 4-benzyloxy-3-carboxy-2-methyl-1-phenylpyrazol-5-one (IX), m. 171° (decompn.), pKa', 3.4. IX decarboxylated as before gave 4-benzoyloxy-2-methyl-1-phenylpyrazol-5-one (X), needles, m. 125-6° (from C6H6-ligroine). IV 4-benzyl ether (0.5 g.) in 15 ml. MeOH treated 5 hrs. at 0° with dry NH3 gave 0.45 g. 4-benzyloxy-3-carbamoyl-2-methyl-1-phenylpyrazol-5-one (XI), m. 120.5-1.5°. Reduction of 0.75 g. XI with Pd-SrCO3 gave 0.2 g. of the hydroxyamide (XII), m. 246° (decompn.), pKa' 6.0. VIII (1 g.) in alc. refluxed 3 hrs. with 2 ml. N2H4.H2O gave the hydrazide (XIII), needles, m. 115°. Hydrogenation of XIII gave 0.2 g. of the hydroxy hydrazide (XIV), plates, m. 214° decompn.). IV (13 g.) with CH2N2 and then with AcOH gave 11.6 g. 3-ethoxycarbonyl-4-methoxy-2-methyl-1-phenylpyrazol-5-one (XV), m. 77° (from ligroine). Hydrolysis of 6 g. XV afforded 4.6 g. 3-carboxy-4-methoxy-2-methyl-1-phenylpyrazol-5-one (XVI), m. 185° (decompn.). Heating XVI at 185° gave 4-methoxy-2-methyl-1-phenylpyrazol-5-one (XVII), prisms, m. 118-20° (from C6H6-ligroine). XVII was also obtained from VI by the action of CH2N2. XV (7 g.) in Et2O added dropwise to 2 moles LiBH4 suspended in 25 ml. tetrahydrofuran, the mixt. left 0.5 hr., and distd. to dryness gave 4.1 g. 3-hydroxymethyl-4-methoxy-2-methyl-1-phenylpyrazol-5-one (XVIII), needles, m. 155° (from H2O). Dry NH3 bubbled into 10 g. XV in 30 ml. MeOH 4 hrs. at 0° gave 6.7 g. 3-carbamoyl-4-methoxy-2-methyl-1-phenylpyrazol-5-one (XIX), m. 125°. XIX (1 g.) and 1 g. P2O5 mixed and distd. gave 0.5 g. 3-cyano-4-methoxy-2-methyl-1-phenylpyrazol-5-one, plates, m. 89-90°. IIIb (2 g.), 15 g. MeI, and 5 ml. MeOH heated 15 hrs. at 110° in a sealed tube gave 0.3 g. 3-ethoxycarbonyl-4-hydroxy-2-methyl-1-p-nitrophenylpyrazol-5-one (XX), cubes, m. 225-56° (decompn.); acetate, yellow prisms, m. 117.5-18.0° (from C6H6-ligroine). XV (19 g.) in C6H6 added dropwise during 15 min. to a cooled suspension 2.75 g. LiAlH4 in Et2O, the mixt. refluxed 4 hrs., and decompd. gave 8.8 g. 3-hydroxymethyl-4-methoxy-2-methyl-1-phenylpyrazolid-5-one, b0.2 149-51°, nD20 1.5600. Antipyrine (100 g.) in C6H6 reduced with 20 g. LiAlH4 in Et2O as above gave 60 g. of 2,3-dimethyl-1-phenyl-Δ3-pyrazoline (XXI), b0.2 58°, nD20 1.5708, pKa' 3.72; sulfate, m. 160°. Hydrogenation of XXI over Pd-C gave 2,3-dimethyl-1-phenylpyrazolidine, b0.3 68.5°, nD20 1.5511, pKa', 4.28. Dihydroantipyrine was also isolated from the reduction as a viscous oil (14 g.), b0.4 112-14°, nD20 1.5571, pKa', 9.05. IIb (5.4 g.) in 100 ml. alc. reduced with Pd-C gave 3 g. N-anilinomandelamidine (XXII), prisms, m. 132-4° (from 50% aq. alc.); hydrochloride, needles, m. 210° (decompn.). Refluxing Et mandelimidate-HCl (43 g.) and 21.6 g. PhNHNH2 0.5 hr. in alc. gave 35 g. XXII HCl salt. IIa (4.8 g.) in alc. hydrogenated at atm. pressure with Raney Ni W6, the catalyst removed, the soln. evapd. to dryness, and the residue refluxed 4 hrs. with 25 ml. H2O gave 15% of a mixt. of IIIa and III, m. 222-4° (decompn.). Ultraviolet spectra are given for II, IV, V, VI, VII, VIII, IX, X, XI, XII, XIV, XV, XVI, XVII, XVIII, XX, and XXII.

IT 100961-92-0P, Cinnamonitrile, α-phenylazo-

L6 ANSWER 70 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
RL: PREP (Preparation)
(prepn. of)
RN 100961-92-0 CAPLUS
CN Cinnamonitrile, α-phenylazo- (6CI) (CA INDEX NAME)



L6 ANSWER 71 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1955:35975 CAPLUS
DOCUMENT NUMBER: 49:35975
ORIGINAL REFERENCE NO.: 49:6929h-i,6930a-i,6931a-h
TITLE: Chroman and isochroman, synthesis of chromenes
AUTHOR(S): Maitte, Pierre
SOURCE: Ann. chim. (Paris) (1954), 9, 431-75
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 49:35975

AB The syntheses of unsubstd. 1(4H)-benzopyran (I) and 1(2H)-benzopyran (II) has been accomplished but the corresponding 1H-2-benzopyran (isochromene) is still unknown, o-Propenylphenol (III) did not give I, but the introduction of the double bond into chroman (IV) succeeded, o-Allylphenol (V), heated above 300° over Al2O3 gives mainly 2-methylcoumarin, with traces of IV, and some III. III is made from V with EtOK. III and V treated with N-bromosuccinimide (VI) gave the same product; decomposition of this compound with EtONa gives α-ethoxy-o-allylphenol. PhONa and CH2:CHCH2Cl 5 mol each gave 540 g. PhOCH2CH:CH2 (VII), b15 84°, and 20 g.V. VII refluxed 6 h. and distilled gave 930% V, b. 218°. V 100, KOH 125, and EtOH 300 parts are refluxed 24 h., the alc. distilled off, H2O, added, the aqueous layer decanted, acidified, extracted with Et2O, and the extract dried, and distilled, gave III, b. 114-15°, m. 37°. The acetate of III (or V) was brominated 12 h. in CCl4 with the calculated amount of recrystd. VI, CCl4 was distilled off, and the product crystalline at 0° to give 60% of a product which is only stable a few days, m. 79.5-80° (C6H6-petr. ether). The cyclization attempt with KOH gave a resin-like residue, the reaction with 2.5 mol Et2NH gave o-[α-(diethylamino)allyl]phenol. The same bromination of o-estragole (VIII) and o-anethole gave α-bromoallyl-o-anisole (IX) in both cases. Treatment with EtONa 1.2 mol gave in 6 h. α-ethoxyallyl-o-anisole (X), b0.7 104-5°, b12 146-7° d12 1.075, nD13 1.5504. X reduced catalytically with Raney Ni (XI) gave after 3 h. α-ethoxypropyl-o-anisole (XII), b13 125-6°, d13 0.996, nD13 1.5060. Bouveault-Blanc reduction of X gave VIII and very little o-PrC6H4OMe. X 1 part with 1.25 part EtOK and 3 parts EtOH gave α-ethoxypropenyl-o-anisole, b14.5 138-9° d17 1.0235, nD17 1.5252; reduced to XII with XI. IX with Et2NH gave α-diethylaminoallyl-o-anisole, b14 143-5°; picrate, m. 124.5°. An improved preparation for IV is given. PhOCHCHCH2Cl (300 g.) was heated with 30 g. SnCl4 to 190-205° for 6 h., the black product cooled, dissolved in 300 cc. HCl 1:1 extracted with 300 cc. Et2O, dried with Na2SO4, distilled, and, after treatment with Na to destroy the chloroether, distilled again to give 85% stable IV, b760 215°, b12.5 89°, m. 4.8°, d16 1.066, nD16 1.5505. From p-cresyl γ-chloropropyl ether [Blank, Ber. 95, 3045(1892)] the same method yielded 85% 6-methylchroman, b14 104°, d16 1.0412, nD16 1.5441. p-BrC6H4OCH2CH2CH2Cl, b10.5 153.5° gave 6-bromochroman (XIII), b16 141°, d21 1.4972, nD21 1.5914, and p-ClC6H4OCH2CH2CH2Cl, b13 146-7° gave 6-chlorochroman (XIV), b15 123°, d14.5 1.220, nD14.5 1.5648. Cyclization of the p-O2N derivative (b0.7 153-4°, m. 39° d16 1.2972, nK 1.5855) of VII, VII itself, or PhOCH2CHClCH2Cl failed. The bromination by dropwise addition of Br to a solution of 0.1 mol IV in 50 cc. CCl4 until the solution becomes pink yielded 87% XIII. With Cl a mixture of XIV, dichlorochroman (b6 112-14°) and trichlorochroman (b6 122-4°) was obtained. Heating IV (0.4 mol), 0.2 mol SO2Cl2, and

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0.5 mol BzOZH in 50 cc. CCl4 to boiling and distg. off CCl4, excess SO2Cl2, and HCl gave 80% XIV, free of other chlorinated compds. IV treated with VI gave partly 4-bromochroman (XV) which was converted with Et2NH (150% excess) into 4-diethylaminochroman, b16 143.5°, d22 1.0136, nD 1.5252, and very little II. With Grignard reactions the following compds. were made: 4-ethylchroman, b15 113° d18 1.0275, nD18 1.5416; 4-propylchroman, b13 128°, d20 1.081, nD20 1.5434; 4-butylchroman, b15 141°, d20 1.061, nD20 1.5387; and 4-phenylchroman, b0.6 123°, d2.5 1.1208, nD21.5 1.6035. Coumarin reduced with XI at 60° and under 90 atm. yielded dihydrocoumarin, b15 147°. This was treated with BuMgBr, decompd. with ice and NH4Cl, giving, after cyclization with 10% H3PO4, 70% 2,2-dibutylchroman, b17 173° b0.8 123°, nD15 1.5121 (cf. Smith and Ruoff, C.A. 34, 1661.7). The mixt. of XIII and XV was added dropwise to a cooled soln. of EtONa (20-30% excess) in alc., refluxed slightly, the alc. evapd., the residue taken up in H2O, extd. with Et2O, the ext. dried with Na2SO4, and a fast distn. gave a fraction b15 120-30°, contg. mainly 4-ethoxychroman, b0.4 93-4° d15 1.081, nD15 1.5340. Slow distn. gave decompn. at 15 mm. from 91-3°, forming II, b15 92-2.5°, b13 91°, d16 1.0993, nD16 1.5923. Bromination of II in CCl4 gave the unstable 3,4-dibromochroman (XVI), m. 124-4.5°, which, on treatment with KOH, gave 3-bromo-1,2H-benzopyran, b10 118-20°. II (11 g.) dissolved in alc. 50 cc. and hydrogenated 3 h. with 1750 cc. H over XI gave 100% IV. With small amts. of VI, IV gave XVI in addn. to the above products. Bromination of 2- or 6-subst. IV and further treatment by the same method gave the corresponding 2- or 6-substd. II. The following derivs. of II were prepd. (substituent b.p./mm., dt, nDt, t given): 6-Me, 104°/11, 1.0602, 1.5691, 16° (3,4-dibromo deriv., unstable, m. 84°); 6-Cl, 120°/14.5, 1.245, 1.5976, 17°; 6-Br, 136°/14, 1.5235, 1.6105, 16°; 2,2-di-Bu, 163-4/13.5, 0.9627, 1.5138, 17°. Bromination with VI and dehydrobromination with EtONa gave the following deriv. of II from the corresponding chromans: 4-Et (XVII), 121°/13, 1.064, 1.5776, 20.5°, 4-Ph, 137-8°/0.6, 1.1408, 1.6842, 21.5°. XVII is made from 4-chromanone. 2-Methylcoumaran, b13 119°, was added dropwise to an Al catalyst at 350-400° under N. The resulting mixt. was washed with 20% NaOH, dried, and distd. A neutral fraction b11 75-85° (64%) contained 2-methylcoumaran and I. Several fractionations gave I, b9 77°, d12.5 1.0732, nD12.5 1.5641. I hydrogenated with XI gave IV quant. Stirred with HgCl2 and AcOK, 2-chloromercury-1,4H-benzopyran was obtained, m. 141°. This, decompd. with 5N HCl 12 h. at 50°, washed with NaHCO3, dried, and distd. gave 2-chromanol, b12.5 139°; 2,4-dinitrophenylhydrazone, m. 185° (from EtOH). I refluxed 12 h. with twice its vol. of alc. and one drop HCl gave 2-ethoxychroman, b12 111.5-12°, d22.5 1.0602, nD22.5 1.5208. I absorbs Br immediately, but the 2,3-dibromo deriv. of IV could not be isolated. 3-Bromo deriv. of I b13 119°, nD23 1.557. Phenylethylalc. (230 g.) and 70 g. trimethylene oxide were cooled and a rapid stream of HCl was passed into the stirred emulsion. When the temp. reached 10° in spite of cooling, 2 layers formed, 300 cc. concd. HCl was added with shaking, the temp. rose to 45-50°, the mixt. cooled to room temp., dild. with H2O to twice its vol., and the same vol. Et2O added. The org. layer was washed with NaHCO3 and dried, and the solvent removed (the temp. kept just below the product b.p. for a while then distd.) gave 225 g. pure isochroman (XVIII), b11.5 88° b13 91° d17.5 1.068, nD17.5 1.5478. XVIII was chlorinated at -5°, kept under vacuum a while, and then distd. to give 1-chloroisochroman (XIX), b12.5 128°. With VI, XVIII gave

L6 ANSWER 71 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
1-bromoisochroman (XX) quant. The crude XIX (0.1 mol) was dropwise added to 0.25 mol Et2NH in 50 cc. C6H6. After refluxing 1 h. the mixt. was filtered, the amine dissolved in 1:1 HCl, washed with Et2O, freed with NaOH, dried, and distd. to give 14 g. 1-diethylaminoisochroman, b12.5 128°, d2 1.088, nD21 1.5201. XIX or XX with RONa gave the corresponding 1-alkoxyisochroman (R, % yield, b.p./mm., dt, nDt, t. given): Et (XXI), 77, 117-18°/12.5, 1.0645, 1.5180, 22°; Bu (XXII), 80, 150°/16.5, 1.027, 1.5090, 16°. The following 1-substituted isochromans were prepd. in 70-80% yield by a Grignard reaction (substituent given): Et (XXIII), b12.5 102°, d20 1.0205, nD20 1.5293; Ph (XXIV), m. 87. With 0.3 mol CuCN, 0.2 mol XIX in 100 cc. C6H6 gave the 1-cyano deriv. of XVIII, b12.5 145, d21 1.1462, nD21 1.5431. This, treated with alc. KOH gave colorless crystals of isochroman-1-carboxylic acid amide, m. 151-2°. Crude XIX stirred with H2O gave 3,3'-di(isochroman) oxide, b0.7 175-8, m. 137-8° (from dioxane-pet. ether 1:4). The same product was obtained from XXI or 1-acetoxy isochroman (XXV). XXV was made from XIX and fused AcOK. Catalytic hydrogenation of XVIII with XI at 200° and 150 atm. gave, after several distns., tetrahydroisochroman, b12.5 73°, d20 0.9665, nD24 1.4761, and 2-(o-tolyl)ethanol, b13 115°. The heterocyclic ring of XXIII and XXIV also opened with H and XI at 200° and 200 atm. to form o-propyl-2-phenylethanol, b17.5 140° and o-benzyl-2-phenylethanol, b1 143-3.5° resp. The oxidn. of XVIII with SeO2 in xylene. gave 85% dihydroisocoumarin, b0.4 112°, d18.5 1.203, nD18.5 1.5664. XXV decomp. over an open flame at 230°. When XXI and XXII were pyrolyzed at 540° in a N stream only PhEt and EtOH or BuOH and o-CH2:CHC6H4CHO were identified. XVIII (8.5 g.) absorbed 1290 cc. H within 10 min. with XI at room temp., and yielded o-EtC6H4CHO. The latter, treated with Ag2O gave o-EtC6H4CO2H. All attempts to make unsubstd. 1H-2-benzopyran (isochromene) therefore failed. The new compds, are all given with their Raman spectra.

IT 519015-28-2P, Acrylonitrile, 3-(2,4-dimethoxyphenyl)-2-(p-methoxyphenyl)-
RL: PREP (Preparation)
(preparation of)

RN 519015-28-2 CAPLUS

CN Benzeneacetonitrile, α-[(2,4-dimethoxyphenyl)methylene]-4-methoxy- (9CI) (CA INDEX NAME)

L6 ANSWER 72 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1955:23851 CAPLUS
DOCUMENT NUMBER: 49:23851
ORIGINAL REFERENCE NO.: 49:4618c-e
TITLE: Synthesis of a polyamide from furfural. II. Experiments on the ring cleavage of the furylidene system
AUTHOR(S): Okawara, Makoto
CORPORATE SOURCE: Naniwa Univ., Sakai
SOURCE: Kogyo Kagaku Zasshi (1953), 56, 90-2
CODEN: KGKZA7; ISSN: 0368-5462
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. C.A. 47, 4832h. The compds. having the grouping 2-(2-furyl)vinyl or 2-(2-furyl)-2-hydroxyethyl were synthesized and heated with addition of acid in order to obtain alicyclic 4-keto carboxylic acid derivs. 2-(2-Nitrovinyl)furan (I) was prepared from furfural and MeNO2 with NaOH catalyst: I heated with 20 parts concentrated HCl gave 6-nitro-4-oxocaproic acid. An unknown compound (obtained by ring cleavage of difurfurylideneacetone), leaflets, m. 152-4°, showed a mol. weight of 272. Similarly, the ring cleavage reactions were tried for 2-furanacrylonitrile, m. 127°, prepared from furfural and MeCN; 1,2-dihydroxy-1,2-difurylethane, needles, m. 130-1°, prepared by hydrogenation of furoin in EtOH at 65°, followed by vacuum distillation, and other derivs.

IT 7187-01-1P, 2-Furanacrylonitrile
RL: PREP (Preparation)
(preparation of)

RN 7187-01-1 CAPLUS

CN 2-Propenenitrile, 3-(2-furanyl)- (CA INDEX NAME)

L6 ANSWER 73 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1955:15679 CAPLUS
DOCUMENT NUMBER: 49:15679
ORIGINAL REFERENCE NO.: 49:3003c-i
TITLE: Acetylene derivatives. CLXV. Cyanoethylation of acetylenic alcohols and glycols
AUTHOR(S): Nazarov, I. N.; Shvekhgeimer, G. A.
SOURCE: Zhurnal Obshchei Khimii (1954), 24, 157-63
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. C.A. 42, 7732g. Addition of 26.5 g. CH2:CHCN over 1 h. at below 35° to 42 g. Me2C(OH)C.tplbond.CH and 3 g. 40% KOH, stirring 6 h. at room temperature, allowing the mixture to stand overnight, neutralization with 1:1 HCl, filtration, from KCl and distillation gave 57.5 g. Me2C(OCH2CH2CN)C.tplbond.CH (I), b18 96-6.5°, nD20 1.4356, d20 0.9275. Hydrogenation of this (25 g.) in MeOH saturated with NH3 over Raney Ni at 100-10° and 140 atmospheric H pressure gave 24.2 g. Me2EtCOCH2CH2CH2NH2 (II), b14 68-70°, nD20 1.4360, d20 0.8589. I (30 g.), 50 mL. H2O and 100 mL. dioxane treated with stirring with 3 g. HgSO4 and 2 drops H2SO4, then stirred 6 h. at 90° gave, after saturation with Na2CO3 and extraction with Et2O, 26.8 g. Me2CAcOCH2CH2CN, b18 132-6°, nD20 1.4357, d20 1.0033. Similar reaction of 54 g. Me2C(OH)CH:CH2 (III), 3.5 g. 40% KOH, and 35 g. CH2:CHCN gave 32.5 g. Me2C(OCH2CH2CN)CH:CH2 (IV), b16 94-6°, nD20 1.4337, d20 0.9056, and 33 g. initial ROH. Reaction of 42 g. III and 26.5 g. CH2:CHCN with 0.6 g. Na catalyst gave 43.2 g. IV and 8 g. initial ROH. Hydrogenation of the product in MeOH over Raney Ni gave 100% II, b7 56-8°. Reaction of 165 g. Me2C(OH)C.tplbond.CCH:CH2, 10 g. 40% KOH, and 53 g. CH2:CHCN gave 129.5 g. Me2C(OCH2CH2CN)C.tplbond.CCH:CH2, b6 93-4°, nD20 1.4710, d20 0.9334, which hydrogenated to Me2BuCOCH2CH2CH2NH2 (V), b18 102-4°, nD20 1.4485, d20 0.8630. Reaction of 88 g. Me2EtCOH, 2 g. powdered MeONa, and 53 g. CH2:CHCN (temperature rise to 40°, followed by stirring 4 h. at room temperature and standing overnight) gave 14 g. Me2EtCOCH2CH2CN (VI), b18 92-7°, nD20 1.4247, d20 0.8981, and 72.5 g. initial ROH; when 57 g. Me2EtCOH and 4 g. 40% KOH was treated with 35 g. CH2:CHCN no heat was evolved and the mixture was stirred 1 h. at 80°, cooled and neutralized, yielding 3.6 g. VI. Hydrogenation of this over Raney Ni gave 90% II, b7 56-8°. To 120 g. Me2BuCOH was added 1.5 g. K and 53 g. CH2:CHCN was added with cooling; after 2 h. the mixture was neutralized with HCl and treated as usual, yielding 24.3 g. Me2BuCOCH2CH2CN, b11 105-7°, nD20 1.4306, d20 0.8825; the same reaction run with 40% KOH catalyst gave a lower yield; hydrogenation over Raney Ni gave V, b6 78-81°, nD20 1.4482. To 101 g. (.tplbond.CCH2OH)2, 150 mL. dioxane, and 7 g. 40% KOH was added with cooling 125 g. CH2:CHCN below 35°; after 4 h. stirring at room temperature, 48 h. standing, and neutralization with HCl there was obtained 216 g. (.tplbond.CCH2OCH2CH2CN)2, b3 189-95°, nD20 1.4760, d20 1.0910, which hydrogenated as above in MeOH saturated with NH3 over Raney Ni yielding (CH2CH2OCH2CH2CH2NH2)2, b4 134-6°, nD20 1.4618, d20 0.9620. Addition of 50 g. CH2:CHCN to 59 g. (.tplbond.CCMe2OH)2, 200 mL. dioxane, and 4 g. 40% KOH gave no thermal effect; the mixture stirred 5 h. at 60-70° and 1 h. at 70-5°, allowed to stand 40 h., neutralized with HCl and worked up as usual yielded 37.6 g. HOMe2CC.tplbond.CCMe2OCH2CH2CN, b3 111-12°, nD20 1.4530, d20 0.9758, 32.1 g. (.tplbond.CCMe2OCH2CH2CN)2, b2.5 142-6°, nD20 1.4553, d20 0.9915, m. about 25° (after long standing), and 7.9 g. intermediate fraction. Hydrogenation as above over Raney Ni

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gave, resp., HOCH2CH2CH2CH2OCH2CH2CH2NH2, b4 91-4°, nD20 1.4587, d20 0.9321, and (CH2CH2OCH2CH2CH2NH2)2, b3.5 136-8°, nD20 1.4752, d20 0.9539.
IT 107-13-1, Acrylonitrile
(reaction with acetylenic alcs. and glycols)
RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)

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ACCESSION NUMBER: 1951:55473 CAPLUS
DOCUMENT NUMBER: 45:55473
ORIGINAL REFERENCE NO.: 45:9459h-i,9460a-i,9461a-i,9462a-i,9463a-e
TITLE: Formation of nitriles. I
AUTHOR(S): Kurtz, Peter
CORPORATE SOURCE: Farbenfabriken Bayer, Werk Leverkusen, Germany
SOURCE: Ann. (1951), 572, 23-82
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 45:55473
GI For diagram(s), see printed CA Issue.
AB The following members of the research and tech. staffs also contributed materially to this extensive study: W. Lehmann, F. Lober, H. F. Piepenbrink, H. Schwarz, F. Moller, R. Schroter, R. Ludwig, A. Casper, H. Haberland, J. Heinen, D. K.hivin.astner, T. Konig, G. Manz, R. Stroh, H. Wolz, H. Brock, K. Sigwart, and H. Weber. More than 270 literature refs. are given, many of them to German patents, and the following subjects are discussed in a lengthy introduction (pp. 23-52): the addition of HCN (I) to unsatd. esters and nitriles; the formation of esterified α-HO nitriles; the addition of I to unsatd. sulfones and nitro compds.; the addition of I to C2H2 and substituted acetylenes; chemical reactions of NCCH:CHCH:CH2 (II); and the interaction of I with CH2:CHCH2OH and related compds. A number of previously prepared compds. are included (full refs. to which are given in the extensive bibliog.). To 300 g. CH2:CHCN and 3 g. KCN was added (in 1 portion) 1/3 of the equimolar amount of (anhydrous or highly concentrated) I, the mixture warmed to 30°, maintained (after the incipient reaction) at 55-60°, 2/3 of the equimolar amount of I added dropwise (with cooling as required), the mixture warmed 2 h. at 60-70°, and the resulting brown mass was distilled directly in vacuo, giving 420 g. (93%) (CH2CN)2 (III), b10 136°, m. 55°, and 25 g. resinous residue. The above reaction also took place in pyridine (without KCN addition), giving 86% III. When it was carried out on a large scale, a certain amount of crude III (from prior runs) was kept in the reaction vessel, with fresh KCN added, and both the CH2:CHCN and I added dropwise to the mixture; under these conditions yields of 96% III could be reached. By analogous slightly modified procedures (with either K2CO3 or KCN) the following esters of NCCH2CH2CO2H were prepared from the appropriate CH2:CHCO2R (IV): 73% Me, b11 100-1°; 80% Et, b19 111-12°; 78% Bu, b10 123° (yields based on IV entering the reaction). By thermal degradation, Me2C(OAc)CN gave AcOH and CH2:CMeCN, b760 88-90°, which, refluxed with I (and small amts. of KCN) at 40° gave about 1.8% NCCH2CHMeCN (V), b14 120-30° (hydrolyzed by HCl at 110° to HO2CCH2CHMeCO2H, m. 110-12°). V (5%) was also formed from 40 g. mixed cis- and trans-MeCH:CHCN with 17.5 g. I and 0.3 g. KCN; in 20% yield (b0.5 89-91°) by the action of anhydrous I and KCN on CH2:CHCH2CN, and in 26% yield when I in the last named reaction contained small amts. of H2O. Tech. CH2:CMeCO2Me (90.5 g.) refluxed 15 h. with 26 g. I and 2 g. KCN gave 6 g. NCCH2CHMeCO2Me, b11 90°. MeCH:CHCO2Et (80 g.) by an analogous reaction gave 2 g. (slightly impure) NCCHMeCH2CO2Et, b18 105-10°. Δ3-Tetrahydrobenzonitrile, PhCH:CHCN, and PhCH:CHCO2Et all failed to react with I (and KCN). Pyrolysis of PhCMe(OAc)CN gave the easily polymerized PhC(:CH2)CN, b0.4 74-6°, 10 g. of which with I and KCN gave 7.8 g. PhCH(CN)CH2CN, m. 68-9° (after crystallization from alc. and H2O). MeOCH2CH:CHCN by analogous condensation with I gave MeOCH2CH(CN)CH2CN, b0.1 101-4°. ClCH2CH:CHCN was converted into the AcO analog, b11 96-99°; the

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latter with I and KCN formed small amts. of an undistillable resin. Me2NCH2CH:CHCN, b17 64-66° (picrate, m. 124°), also yielded resinous products and HNMe2. 1-Cyano-4-(1-piperidyl)-2-butene (Va), b14 130-1° (picrate, m. 98°), was prepd. by the condensation of piperidine and II; yield 86%. II, b50 58-62°, was formed as follows: I + MeCH:CHCHO →Ac2OH2SO4 76% MeCH:CHCH(CN)OAc, b14 87-92° →500-200°pyrolysis 60-70% II. Va (50 g.) and 9 g. I gave 51% CH2.CH2.CH2.CH2.CH2.NCH2CH2CH(CN)CH2CN, b0.8 146-54°, (picrate, m. 142-44°). Va heated with I and small amts. of KCN gave rise to much polymn., and the expts. were often not reproducible. The mixt. of Va and I heated 6 h. at 45-50° and 10 h. at 65-70° gave very small amts. of (:CHCH2CN)2 (VI), m. 72-3° (from C6H6-petr. ether). In another expt., the mixt. heated 6 h. at 95-100° gave, besides a large resinous residue, a yellow oil, b14 150-80°, which (presumably) contained the isomer NCCH:CH2CH2CH2CN, because on Pd-C catalytic hydrogenation, in MeOH, the mixt. gave an oil, b14 160-70°, which with HCl at room temp. gave (CH2CH2CONH2)2, m. 218-20°. MeCH:CHCH:CHCO2H (prepd. from tech. cyanosorbic acid by decarboxylation) failed to give any definite condensation product with I. Under the usual conditions, HC.tplbond.CCO2Me and I gave 24% NCCH:CHCO2Me, b14 95-7°, m. 35-6° (from Et2O-petr. ether) [readily sapond. to fumaric acid, m. 286-7° (decompn.)]. MeCH:C(CO2Et)2 with I gave 92% MeCH(CN)CH(CO2Et)2, b10 141-3°. On the other hand, PhCH:C(CO2Et)2 (81 g.) and I gave largely the starting material (71.5 g.) and about 10 g. of an uncrystallizable resin contg. 5.45% N (C15H17O4N requires 5.1% N). Di-Me maleate (150 g.) and I gave 33.2 g. of an oil, b0.8 180-184°, which crystd. very gradually but could not be recrystd. and was evidently NC[CH(CO2Me)]3CH2CO2Me; it gave no FeCl3 reaction, was insol. in aq. Na2CO3, and on hydrolysis with HCl at 90° (and finally at 120-30°), followed by evapn. to dryness and heating with Ac2O gave an anhydride, m. 240-42°, which with boiling H2O yielded meso-[HO2CCH2CH(CO2H)]2, m. 188-9°. Condensation of NCCH:CHCH2CN (VII) with I, and extn. of the product with AcOEt, followed by washing with aq. H2SO4 and H2O, drying, and evapn. gave an (unanalyzed) oil (probably an adduct) which decompd. and resinified when heated in a high vacuum. VII (30 g.) on standing 24 h. at room temp. with 65 g. H2SO4 and 210 g. MeOH, followed by heating gradually to 130° and maintaining 4 h., gave after (a fully described) purifn. 37.2 g. di-Me ester of VII, b15 113-14°, 33 g. of which with I (and KCN) gave 3.5 g. (unanalyzed and uncharacterized) NCCH(CH2CO2Me)2 (?), readily sapond. to HO2CCH(CH2CO2H)2, m. 159-60°. From appropriate esters of the type CH2:CHO2CR by addn. of I, the following cyano compds. of the type RCO2CH(CN)Me were prepd. (R is given): 43% H, b15 60-1°; 82% Me, b11 61-2°; 47% Ph, b11 138-40°; and 41% Me2CHCH2CH2, b10 95-6°. MeCH:CHCO2CH:CH2 (150 g.) with 2 g. KCN and 40 g. HCN, yielded 2 compds., sepd. on repeated fractionation: 13.2 g. MeCH:CHCO2CHMe(CN), b11 91-2°, and 34 g. MeCH(CN)CH2CO2CHMe(CN), b0.25 116° (the latter on sapon. forming HO2CCHMeCH2CO2H, m. 110-12°). Compds. of type RCH(OAc)2 or RCH(O2CEt)2 heated at about 140-150° with dry KCN (or NaCN) gave inseparable mixts. of the starting product and the corresponding R'CO2CH(CN)R. Thus from 100 g. MeCH(OAc)2 was formed 67 g. of a mixt. (contg. 8.8% N instead of the theor. 12.38%), b20 73°; from MeCH(O2CEt)2, a mixt. b13 70-2° (contg. 7.35% N instead of 11.02%); from H2C(OAc)2, a mixt. b10 62-66°, contg. AcOCH2CN (10.5% N instead of 14.14%); from Me2CHCH(OAc)2, a mixt., b12 75-77° (contg. 5.3% instead of 9.92% N); PhCH(OAc)2 gave a mixt. contg. PhCH(OAc)CN, b12 131° (which when hydrolyzed with HCl yielded PhCH(OH)CO2H, m. 117-18°). AcOCH:CH2CH:CH2 and I (with KCN), 6 h. at

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95-100°, gave 57% AcOCH(CN)CH:CHMe (or AcOCH(CN)CH2CH:CH2), b20 85-88°. Similarly CH2:C(O2CEt)CH:CH2 yielded much resin and 15% EtCO2CMe(CN)CH:CH2, b14 90-3°. To 6 g. I and 0.5 g. KCN were gradually added 30 g. EtSO2CH:CH2 with the (outer) temp. maintained at 24-32°, during the addn. and then 2 h. at 50°. The reaction product, a viscous oil (presumably EtSO2CH2CH2CN), b0.5 160-8° (partial decompn.), was never obtained pure (KCN, admixed with EtSO2CH:CH2 induced rapid exothermic polymn.). By heating 27 g. O2S.CH2.CH2.CH:CH with 1 g. KCN and 8 g. I, 16 h. at 35-40°, SO2.CH2.CH2.CH(CN).CH2, m. 118°, was formed. O2S.CH2.CH:CH.CH2 apparently does not add I. [p-MeC6H4SO2CH:CH2, however, formed 71% MeC6H4CH2CH2CN, m. 94-5°.] PrCH:CHNO2 added HCN, forming the pale yellow PrCH(CN)CH2NO2, oil, b14 133-5° (the yield of which could not be detd., because of an explosion occurring after about 1/3 of the crude product had been distd.). The following method was adopted for the prepn. of CH2:CHCN (VIII): Into a well-stirred mixt. of 300 g. Cu2Cl2, 100 g. NH4Cl, 5 cc. concd. HCl, 200 cc. H2O, and small amts. of Cu powder at 90° was gradually introduced over 3.5 h. a mixt. of 60-70 l. C2H2 and 20 g. I. The yields of VIII (purified by fractionation) varied from 32 to 88%, but the contact soln. remained active for at least 14 successive runs. (The highest yield of VIII was obtained in the 14th run). VIII was fully identified by the formation of several derivs. (not analyzed), including conversion into III. The still residues (about 600 g.) from the various prepns. of VIII were fractionated in vacuo; of these 289 g. (b30 below 35°) was largely VIII. A fraction b30 35 to b15 80° (48 g.) when steam-distd., Et2O-extd., and fractionated gave 5 g. II, b38 54-59° (identified through the picrate of Va m. 98°) and in the residue from the steam distillate, MeCH(OH)CN, b14 80-90°. Chloroprene was also probably present as an impurity in crude VIII. The following consts. of VIII were detd.: b760 77.6-7.7°, heat of combustion 415.8 kcals./mol, heat of vaporization 0.136 kcals./g. The vapor pressures of VIII (at temps. from -16° to 78.8°) were detd., as were the solubilities of VIII in H2O (at -20 to 84°) and of H2O in VIII (at 0° to 66°) (data for which are tabulated). To a contact mixt. of 1100 g. Cu2Cl2, 590 g. NH4Cl, 950 cc. H2O, 25 cc. HCl, and 30 g. Cu powder at 80° was added dropwise a mixt. of 44 g. CH2:CHC.tplbond.CH and 40 g. HCN. The temp. of the mixt. rose to 50° (after 5 h.); the mixt. was kept at this temp. 10 h., then warmed further by means of a gentle N stream, the condensate extd. with Et2O, and the ext. washed, dried, and fractionated, giving 11.7 g. (17%) II, b44 56-60° (identified as picrate of Va, m. 98°). By an analogous reaction, with a similar contact agent, 160 g. PhC.tplbond.CH gave 1.5 g. (impure) PhCH:CHCN, b12 115-35° (hydrolyzed to PhCH:CHCO2H). Heating 20 g. II and 21 g. H2C:CMeCMe:CH2 [stabilized with p-C6H4(OH)2] 1 h. at 140° gave 19 g. of an adduct, C11H15N, b1.5 82-7°. Similarly 27 g. II and 30 g. chloroprene at 100° gave 7 g. of an adduct, C9H10NCl, b13 141-51°. Dropwise addn. of 100 g. II to 140 g. MeOH contg. MeONa (from 2 g. Na) at 50-60° gave 39% MeOCH2CH2CH(OMe)CH2CN, b17 109-11°, which, hydrogenated in MeOH contg. NH3, with Raney Ni at 110 atm. pressure, gave 85% MeOCH2CH2CH(OMe)CH2CH2NH2, b15 87-91°, giving no cryst. Bz deriv. or picrate. II (100 g.) in 500 cc. MeOH satd. with NH3, let stand 6 days at room temp., and evapd., gave a viscous pale brown oil (H2O-sol.), decompg. on distn., contg. about 22.85% N (possibly C15H18N4). II (100 g.) in 50 cc. THF and 250 cc. liq. NH3, hydrogenated in the presence of Ni-fuller's earth at 70-120°, gave, after fractionation, 24 g. (slightly impure) H2N(CH2)4CN, b12 92-3°; Bz deriv., m. 57-9°. With Raney Ni as catalyst, II in THF and liq. NH3 hydrogenated gave a large amt. of resin, some AmNH2, and 6 g. H2N(CH2)5NH2, b12 75-80° (di-Bz deriv., m.

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130-31°). II (50 g.) added rapidly to 170 g. 50% aq. EtNH2 and heated 5 h. at 50° gave 48.6 g. of a liq., b12 120-24° (slight decompn.), contg. about 23.3% N (presumably a mixt. of C7H12N2 and C9H19N3) and 31.7% of a dark resin. From aq. Me2NH (400 g. 48% soln.) and 216 g. II at 80° was formed an oily mixt., which, when extd., distd., and retreated with 300 g. Me2NH soln., yielded 217 g. Me2NCH2CH2CH(NMe2)CH2CN (IX), b10 120-22° (picrate, m. 122-3°). By a slightly modified procedure, 100 g. II gave, besides IX, 67.6 g. Me2NCH2CH:CHCH2CN, b15 86-96°, which, hydrogenated in NH3-MeOH (with Ni and fuller's earth), yielded Me2N(CH2)5NH2 (Au salt, m. 168°). Et2NH (in excess) reacted vigorously with II, giving as the only product 81% Et2NCH2CH:CHCH2CN (X), b15 107-14° (picrate, m. 96°), which when heated in a bomb tube at 120-30° decompd. and resinified. X hydrogenated with Pd-C gave Et2N(CH2)4CN, b15 108-12° (picrate, m. 86-8°). On more vigorous hydrogenation (with Ni-fuller's earth) X in NH3-MeOH at 90-120° gave Et2N(CH2)5NH2 (XI), b14 95-8° (picrate, m. 129-30°); p-O2NC6H4CO deriv., m. 84-4.5° (from petr. ether). The constitution of the adduct X was indicated by the following synthesis of XI: 1-benzoylpiperidine →PCl3BzNH(CH2)5Cl →Et2NH BzNH(CH2)5NEt2 →HCl bomb tubeXI. II with N2H4.H2O in MeOH (with cooling) gave in good yield H2NNHCH2CH:CHCH2CN, b4.5 131-5° (Bz deriv., m. 231-2°). Similarly II and Me2NNH2 gave Me2NNHCH2CH:CHCH2CN, b12 110-17°. To 50 g. II and 1.5 g. Na2S at 60-70° was added in a rapid stream 11.5 g. H2S, yielding a viscous oil, which, dissolved in C6H6, washed successively with aq. H2SO4 and H2O and freed from C6H6 in vacuo, gave (nearly pure) (NCCH2CH:CHCH2)2S (XII), decompg. on attempted fractionation; when heated 5 h. with concd. HCl, it gave a mixt. of stereoisomeric unsatd. dicarboxylic acids, C10H14O4S, m. 152-5°. To 60 g. HSCH2CO2Et and 0.5 g. KOH at 70° was added dropwise 44 g. II, and the product, purified like XII, gave 11.4 g. NCCH2CH:CHCH2SCH2CO2Et, b0.3 136-40°. II and an aq. 30% soln. of NaHSO3 at 90-100° gradually reacted to form NaO3SCH2CH:CHCH2CN (pptd. from the aq. mixt. with MeOH-Et2O); this with Raney Ni in MeOH gave an (uncharacterized) cryst. compd., which with BzCl gave BzNH(CH2)5SO3Na, m. 216-17° (from MeOH). CH2:CHCH2OH (72%)(29 g.) and 14 g. I, 4.5 g. Cu2Cl2, and 2.6 g. NH4Cl, heated 16 h. in a bomb tube at 95-100°, failed to give an adduct, but yielded 23.3 g. CH2:CHCH2CN, b. 114-16°. PhCH2OH treated similarly (but with NH4Br and Cu2Br2 as catalysts) gave no adduct, and formed very little PhCH2CN, the principal product being (PhCH2)2O, b18 160-65°. To a stirred mixt. of 200 g. Cu2Cl2, 150 g. KCl, and 172 cc. H2O, made acid to Congo red and treated with Cu powder, were added over a 6-h. period 352 g. (HOCH2CH:)2 and 224 g. I at 80°, stirring continued 2 h. longer, and the mixt. extd. at 60° with C6H6 and fractionated, yielding as the main (68%) fraction 293 g. crude VI, and 38 g. resin. The contact mixt., after evapn. of the H2O, was reused in subsequent runs (giving 74-75% VI). Purified VI, m. 76° (from EtOH), d80.4 0.953, heat of combustion 811.8 kcals./mol, heat of vaporization, 0.1144 kcals./g. (at 274°, 760 mm.). Sp. heat and solubilities in MePh, xylene, PhCl, EtOH, and H2O (at various temps.) were detd. In the recrystn. of VI, the mother liquors yielded an oily mixt., apparently contg. HOCH2CH:CHCH2CN, or an isomer, inasmuch as hydrogenation in NH4OH with Raney-Co gave H2N(CH2)5OH, b13 114-15°, m. 38° (picrate, m. 94-5°). With Raney-Ni, VI in THF contg. NH3 was hydrogenated to 85% (CH2CH2CH2NH2)2, m. 38-9° (di-Ac deriv., m. 123-4°; di-Bz deriv., m. 157-8°). The action of Cu2Cl2 on VI (at 150° and 200° for 5 h.) with varying amts. of catalyst was studied exhaustively. In general, the lower the

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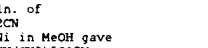
temp., and the lower the % catalyst, the less decompn. (i.e., resin formation) of VI was noted. E.g., at 150°, with 1% Cu2Cl2, VI was completely resinified; with 0.01% Cu2Cl2 at 150°, it was almost quant. recovered; at 200°, it isomerized and/or resinified, unless the catalyst was reduced to 0.01%. (Details are given for removal of residual Cu2Cl2.) When 1 kg. VI and 1 g. Cu2Cl2 were heated 5 h. at 200° and the cooled mixt. extd. with C6H6, filtered, and freed from solvent, the residue (869.5 g.) failed to crystallize and on distn. yielded 2 main fractions, each of which had the compn. C6H6N2 (apparently the cis- and trans-isomers of NCCH:CHCH2CH2CN), b0.9 108-12°, n20D 1.46777, and b0.9 115-118°, n20D 1.46865, together with 116 g. resin. Crude VI with 10% aq. KCN resinified. Various relatively unsatisfactory methods for prepg. VI are outlined. E.g., 300 g. (HOCH2CH:)2 and 95 g. I added slowly to 200 g. Cu2Cl2, 162 g. NH4Cl, 172 cc. H2O, 5 cc. HCl, and 15 g. EtOH, and the mixt. extd. with C6H6 and fractionated gave 61.3 g. EtOCH2CH:CHCH2CN, b12 90-104°, and 60.4 g. VI. To 650 g. Cu2Cl2, 350 g. NH4Cl, 500 cc. H2O, 10 g. Cu powder, and 30 cc. HCl in an atm. of N at 105-110° was added 1 kg. CH2:CHCH2OH at the rate of 100-200 cc./h., and the resulting products promptly distd., extd. with CH2Cl2, and fractionated in a Raschigring column, giving 650 g. (CH2:CHCH2)2O, b. 89.5-91.5°. Very similarly formed were (PhCH2)2O, b14 164-6°, and (by successive addns. of BuOH and allyl alc. to the catalyst) CH2:CHCH2OBu, b. 114-18°; (from (CH2OH)2 and allyl alc.) (CH2:CHCH2OCH2)2, b18 60.5-4°; and (from (HOCH2CH2)2 and allyl alc.), (CH2:CHCH2OCH2CH2)2, b10 84-7°.

IT 1615-70-9, 2,4-Pentadienenitrile
(and adducts)

RN 1615-70-9 CAPLUS

CN 2,4-Pentadienenitrile (CA INDEX NAME)



IT 13042-02-9, α-Hydromucononitrile
(mixture containing)

RN 13042-02-9 CAPLUS

CN 2-Hexenedinitrile (CA INDEX NAME)

IT 107-13-1P, Acrylonitrile 126-98-7P, Methacrylonitrile 495-10-3P, Atroponitrile 2141-59-5P, α-Hydromucononitrile, trans- 4360-47-8P, Cinnamonitrile 44653-08-9P, Acrylic acid, 3-cyano-, methyl ester 90330-08-8P, Crotononitrile, 4-hydroxy-, acetate 101084-47-3P, Crotononitrile, 4-dimethylamino- 856181-87-8P, Crotononitrile, 4-dimethylamino-, picrate
RL: PREP (Preparation)
(preparation of)

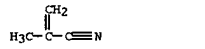
RN 107-13-1 CAPLUS

CN 2-Propenenitrile (CA INDEX NAME)

L6 ANSWER 74 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

RN 126-98-7 CAPLUS

CN 2-Propenenitrile, 2-methyl- (CA INDEX NAME)



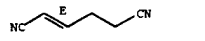
RN 495-10-3 CAPLUS

CN Benzeneacetonitrile, α-methylene- (CA INDEX NAME)

RN 2141-59-5 CAPLUS

CN 2-Hexenedinitrile, (2E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.

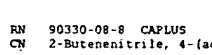


RN 4360-47-8 CAPLUS

CN 2-Propenenitrile, 3-phenyl- (CA INDEX NAME)

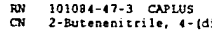
RN 44653-08-9 CAPLUS

CN 2-Propenoic acid, 3-cyano-, methyl ester (CA INDEX NAME)



RN 90330-08-8 CAPLUS

CN 2-Butenenitrile, 4-(acetyloxy)- (9CI) (CA INDEX NAME)



RN 101084-47-3 CAPLUS

CN 2-Butenenitrile, 4-(dimethylamino)- (9CI) (CA INDEX NAME)

RN 856181-87-8 CAPLUS

CN Crotononitrile, 4-dimethylamino-, picrate (5CI) (CA INDEX NAME)

L6 ANSWER 74 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

CM 1

CRN 101084-47-3

CMF C6 H10 N2

CM 2

CRN 88-89-1

CMF C6 H3 N3 O7

L6 ANSWER 75 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1951:8765 CAPLUS
DOCUMENT NUMBER: 45:8765
ORIGINAL REFERENCE NO.: 45:1589f-i,1590a-i,1591a-i,1592a
TITLE: Piperidine and azabicyclo compounds. I. Via Michael condensations
AUTHOR(S): Albertson, Noel F.
CORPORATE SOURCE: Sterling-Winthrop Research Inst., Rensselaer, NY
SOURCE: Journal of the American Chemical Society (1950), 72, 2594-9
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 45:8765

GI For diagram(s), see printed CA Issue.

AB Since so many piperidine compds. show marked physiol. activity, their synthesis, by catalytic reduction to piperidines and bicyclo N compds. of δ-keto nitriles prepared by Michael condensations between vinyl ketones and cyanoacetic esters or between CH2:CHCN (I) and β-ketones, was reinvestigated. Adding 600 mL. AcCH2CO2Et (II) to 3 g. Na in 400 mL. EtOH, followed by 246 mL. I at such a rate that the temperature did not exceed 45°, distilling off the EtOH, washing the residue with H2O containing 10 mL. AcOH, and distilling gave 63% AcCH(CO2Et)(CH2)2CN (III), b2 121°, n25D 1.4446, and a residue of AcC(CO2Et)(CH2CH2CN)2 (C.A. 23,834). Adding 200 g. III to 200 g. Na2CO3 in 1800 mL. H2O, refluxing 4 h., salting out with K2CO3, and extracting with Et2O gave 71% Ac(CH2)3CN (IV), b5.2 86.5°, n25D 1.4790 (2,4-dinitrophenylhydrazone, m. 154-5°). IV may also be prepared from I and Me2CO, but the yield is very low (8.6%) because of polycyanoethylation. β-Keto esters give much higher yields of (CH2)2CN derivs. than do ketones. Reduction of IV with Raney Ni gave 85% MeC.(CH2)4.NH. Addition of 168 g. AcCH(CH2Ph)CO2Et (V) to 0.5 g. Na in 200 mL. 95% EtOH, followed by 53 mL. I at such a rate that the temperature remained at 25-35°, acidification with alc. HCl 0.5 h. after the addition of I, and distillation gave 141 g. (85%) AcC(CH2Ph)(CO2Et)(CH2)2CN, b1.5 172°, n25D 1.5068, and 35 g. V. Use of com. absolute EtOH gave PhCH2CH(CO2Et)(CH2)2CN, b2.0 152°, n25D 1.5002, as major or sole product by loss of an Ac group. Addition of 512 g. CH2.CH2.CHAc.CO.O to 2 g. Na in 300 mL. EtOH, followed by 290 mL. I, acidification of the mixture after 1 h., and allowing to stand 1-2 days gave 86-92% CH2.CH2.CAc(CH2CH2CN).CO.O (VI), m. 44-6° (from MeOH), b1.5 162°, n25D 1.4790, which on refluxing 6 h. with 10% aqueous Na2CO3, salting out with K2CO3, extracting with iso-PrOH, and distilling gave a poor yield of yellow oil, b3.5 115-46° [2,4-dinitrophenylhydrazone, m. 159° (from AcOEt)]. VI (40 g.) hydrolyzed by 80 g. KOH in aqueous MeOH, acidified, extracted with AcOEt, and concentrated gave 22 g. α-(2-hydroxyethyl)glutaric acid lactone, b1.0 163-6°. BzCH(CO2Et)(CH2)2CN (VII) (100 g.), refluxed 10 h. with 100 g. Na2CO3 and 900 mL. H2O, extracted with Et2O, dried, and distilled gave 37.0 g. (52%) Bz(CH2)3CN, b0.1 125°, n25D 1.5326, and 4 g. Bz(CH2)3CONH2 (VIII), m. 140-1° (from H2O). VIII was also prepared by condensing I with AcCHBzCO2Et and hydrolyzing the condensation product with Na2CO3 solution Addition of 122 g. III and 50 mL. MeI to 15.3 g. Na in 300 mL. dry EtOH and working up the mixture in the usual manner after 2 days' standing gave, on distillation, 35.6 g. NC(CH2)2CHMeCO2Et, b0.8 74-80°, n25D 1.4270, and 63.6 g. AcCMe(CO2Et)(CH2)2CN, b0.8 109°, n25D 1.4461. AcC(CHMe2)(CO2Et)(CH2)2CN, b0.1 121° n25D 1.4542, was prepd. in 37% yield by the method of Koelsch and Walker (C.A. 45, 1135f) and in poorer yield from III, iso-Pr2O, and BF3 by the method used by Hauser and Breslow (C.A. 34, 7875.6) to alkylate II. Other keto nitriles, AcCRR'CH2CH2CN, prepd. in a manner analogous to III: (R, R', yield (%), b.p. °C. (mm.), n25D resp., given): CH2CH2CO2Me, CO2Et, 100, 166° (1.7), 1.4510; CH2CH2CO2Et, CO2Et, 82, 168° (0.8), 1.4578; CH2Ph, CO2Me, 56, 163° (0.2), 1.5158; C6H13, CO2Et, 73, 157° (2.9), 1.4511; C7H15, CO2Et, 81, 145° (0.9), 1.4505; iso-Bu, CO2Et, 60, 125° (0.1), 1.4528. Also prepd. were CO.CH2.CH2.CH2.C(CO2Et)(CH2)2CN, 82, 145° (1.5), 1.4663; AcC(CH2CH2CN).CH2.C(CH2Cl).O.CO, 61, 199° (1.6), 1.4982; and BzCH(CO2Et)(CH2)2CN, 86, 176° (0.7), 1.5131. AcC(CH2OH)(CO2Et)(CH2)2CN, n25D 1.4585, was obtained in 94% yield from IV and formalin. Redn. of 93 g. AcC(CO2Et)(CH2CH2CO2Me)(CH2)2CN in 400 mL. EtOH by Raney Ni and H at 100° and 50 lb. pressure for 6 h., removal of the EtOH in vacuo, and filtration from dil. Et2O gave 36% 5-carbethoxy-9-methyl-2-oxo-1-azabicyclo[3.3.1]nonane, m. 170.4-1.3° (cor., from EtOH). The Et2O soln. gave 37.9 g. (43%) Et 3-(2-carbomethoxyethyl)-2-methylnipecotate, b1.4 139°, n25D 1.4740. A soln. of 115 g. Et 2-(2-cyanoethyl)cyclopentan-1-one-2-carboxylate in 400 mL. EtOH reduced by Raney Ni and H at 120° and 400 lb. pressure for 7 h. gave, on distn., 79 g. (73%) 4a-carbethoxyoctahydro-1-pyrindine (IX), b0.6 87°, n25D 1.4799 (cf. Henecka, Fr. 881,360), and 14.7 g. of a yellow oil, b0.4 153-209°, n25D 1.4852-8, m. 52.9-4.8° (cor., from Et2O), which may be the alc. obtained by redn. of the C:O bond. Redn. of 1 mol VI in 400 mL. MeOH by Raney Ni and H at 90° and 500 lb. pressure for 6 h. and treatment of the product with alc. HCl gave 62 g. 1-methyl-2-aza-8-oxaspiro[5.4]decan-7-one-HCl (X), m. 265-6.4° (cor., from EtOH). Hydrogenation of 116.2 g. Et 2-methylnipecotate in 400 mL. EtOH and 68 mL. 37% formalin at 25° and 400 lb. pressure with a buffered Pd-C catalyst required less than 45 min., giving on distn. 122.2 g. (98%) Et 1,2-dimethylnipecotate (XI), b0.2 73°, n25D 1.4557 [methiodide, m. 185.0-6.4° (cor.)]. The following piperidines (Xa) were prepd. in a similar fashion (R1, R2, R3, R4, % yield, b.p. °C. (mm.), n25D, resp.): H, Me, H, H, 85, 117° (760), 1.444; H, Me, H, CO2Et, 86, 59° (0.5), 1.4557 [1-PhNHCO deriv., m. 134.6-6.0° (cor.)]; Me, Me, H, CO2H, -, - (-), - [HCl salt, m. 185.8-8° (cor.)]; H, Me, Me, CO2Et, 89, 63° (0.1), 1.4581 [HCl salt, m. 164.4-5.0° (cor.)]; Me, Me, Me, CO2Et, 58, 67° (0.9), 1.4592; H, Me, iso-Pr, CO2Et, 84, 91° (0.3), 1.4666; Me, Me, iso-Pr, CO2Et, 82, 92° (0.6), 1.4642; H, Me, iso-Bu, CO2Et, 91, 98° (0.3), 1.4658; Me, Me, iso-Bu, CO2Et, 84, 95° (0.9), 1.4612; H, Me, C6H13, CO2Et, 85, 106° (0.2), 1.4627; Me, Me, C6H13, CO2Et, 80, 130° (1.9), 1.4609; H, Me, C7H15, CO2Et, 63, 120° (0.7), 1.4665; Me, Me, C7H15, CO2Et, 33, 136° (1.5), 1.4638; Me, Me, PhCH2, CO2Et, 81, 134° (0.2), 1.5110; H, Me, PhCH2, CO2Me, 78, 137° (0.6), 1.5335; Me, Me, PhCH2, CO2Me, 75, 132° (0.8), 1.5223; H, Me, Ph, CO2Et, 57, 131° (0.3), 1.5323; H, Me, -(CH2)2OCO-, 30, - (-), - (HCl salt, m. 265-6°); Me, Me, -(CH2)2OCO-, 70, - (-), - (HCl salt, m. 72-5°); Me, -(CH2)3-, CO2Et, 85, 83° (1.0), 1.4755; H, Me, (CH2)2CO2Et, CO2Et, 65, 133° (0.9), 1.4740; Me, Me, (CH2)2CO2Et, CO2Et, 86, 128° (1.0), 1.4726; H, Me, (CH2)3NH2, Me, 77, 80° (1.2), 1.5031 (b760 250-5°); di-HCl salt, m. 243-6°; monopicrate, m. 194-5°); H, Ph, H, H, 80, 80° (0.2), 1.5232 (readily hydrated on shaking with H2O); Me, Ph, H, CO2Et, 94, 116° (0.1), 1.5178. Redn. of 90 g. III in 400 mL. EtOH by Raney Ni and H at 60° and 600 lb. pressure for 1-3 h./mol H gave 89-93% 5-carbethoxy-6-methyltetrahydro-2-pyronimine, b0.9 103-6°, n25D 1.5350 (supercooled, solid at room temp.), which loses NH3 on refluxing with HCl and is undoubtedly identical with Henecka's 1-cyanopentan-4-ol-3-carboxylic ester (C.A. 44, 2520c). Redn. of γ-cyano esters with Raney Ni gave only piperidines, usually in high yield, while redn. of III gave 86% XI. These results are in marked contrast to those of Henecka (see above), who stated that III does not give a piperidine on redn. unless first converted to the corresponding β-aminocrotonic ester with NH3. Redn. of 165 g. VII in 335 mL. EtOH with Raney Ni and H at 115° and 700 lb. pressure for 1 h. and distn. gave 113.1 g. (73%) Et 2-phenylnipecotate, b0.08 113°, n25D 1.5227 [HCl salt, m. 202.2-3.4° (cor.); phosphate, m. 183.3-4.9° (cor.)], some BzH, and 19.3 g. of an oil depositing crystals of 5-carbethoxy-6-phenyltetrahydro-2-pyronimine, m. 106.2-8.4° (cor.) (from petr. ether, AcOEt, and iso-PrOH successively). 4-(2,3-Dimethoxyphenyl)-3-buten-2-one (XII), b1.1 135-9°, n25D, 1.5810 (70% yield), and AcCH2CHPhCH(CN)CO2Et, b0.8 160-5°, n25D 1.5102, were prepd. in the usual manner. Addn. of CH(CN)EtCO2Et (XIII) to PhCH:CHAc gave 23% AcCH2CHPhCEt(CN)CO2Et, b1.4 153-61° (decompn.), n25D 1.5050. A soln. of 103 g. XII and 71 g. XIII in 100 mL. EtOH, just basic to EtONa, warmed 2.5 h. on a steam bath, acidified with alc. HCl, concd., and distd. gave 129 g. of an oil, b1.5 55-151°, which on treatment with EtONa and 3 days' standing gave 96.5 g. Et 2-cyano-2-ethyl-3-(2,3-dimethoxyphenyl)-5-oxohexanoate, b1.5-2.4 160-97°, n25D 1.5168 (supercooled), m. 91-4° (from EtOH). Octahydro-4-methyl-1H-quinolizine(?) (HCl salt, m. above 360°; cf. Lukes and Sorm, C.A. 42, 7780d) and 1-(2-piperidyl)-4-pentanol were prepd. by redn. of 1-(2-pyridyl)-4-pentanone by Raney Ni and H at 150° and 250 lb. pressure (Boekelheide and Rothchild, C.A. 43, 4267e). AcCH2Ac (50 g.), 1.5 g. Na, and 108 g. 2-vinylpyridine refluxed 7 h. and distd. gave 14.1 g. 1-(2-pyridyl)-4-pentanone (XIV), b1 84-118°, and 37.4 g. of the 3-Ac deriv. of XIV, b1 118-19°. The following piperidines (XV) were prepd. by the Raney Ni redn. of the keto nitriles in EtOH or by reductive methylation of the piperidines with formalin and a Pd-C catalyst as previously described (R1, R2, R3, b.p. (mm.), n25D, resp.): H, H, Ph, 130° (1.0), 1.5172; Me, H, Ph, 127° (1.5), 1.5104; H, Et, Ph, 131° (1.6), 1.5148; Me,Et, Ph, 118° (0.6), 1.5105; H, Et, 2,3-(MeO)2C6H3, 158° (0.8), 1.5194; Me, Et, 2,3-(MeO)2C6H3, 153° (0.9), 1.5152. Whereas redn. of α-(2-cyanoethyl)acetoacetic esters gave principally piperidines, redn. of Et α-[2-(2-pyridyl)ethyl]acetoacetate in EtOH with Raney Ni at 150° gave 40% Et octahydro-4-methyl-1H-quinolizine-3-carboxylate and 45% octahydro-3-(1-hydroxyethyl)-4-oxo-4H-quinolizine, the piperidone type of ring closure predominating. Of the mols. having more than 1 asym. C atom, only a single dl-modification is obtained on redn. Nearly all these piperidines and bicyclo compds. have been prepd. in only 3 steps from readily available and cheap materials. Some of these compds. show mild analgesic activity.

IT 107-13-1, Acrylonitrile
(reaction with ketones)

RN 107-13-1 CAPLUS

CN 2-Propenenitrile (CA INDEX NAME)

L6 ANSWER 75 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

L6 ANSWER 75 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

L6 ANSWER 76 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1950:22473 CAPLUS
DOCUMENT NUMBER: 44:22473
ORIGINAL REFERENCE NO.: 44:4426e-i,4427a-i,4428a-e
TITLE: Diene synthesis. XXII. The diene synthesis with aliphatic fulvenes
AUTHOR(S): Alder, Kurt; Ruhrmann, Rudolf
CORPORATE SOURCE: Univ. Cologne, Germany
SOURCE: Ann. (1950), 566, 1-27
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 44, 2479c, and Alder and Stein, C.A. 31, 7033.6. Adducts of dimethylfulvene (I) with maleic anhydride (II) can only be of the type (III). Past expts. indicate that addition at other points of I are excluded. The relative amts. of the "exo-A form" (IIIa), needles, m. 137° (from AcOEt) (cf. C.A. 24, 96) and the "endo-B form" (IIIb), rectangles, m. 112° (from AcOH), obtained vary, depending on the conditions of adduct formation. E.g., 5 g. I and 5 g. II in Et2O at 38° gave 3.3 g. IIIa and 2.6 g. IIIb; at 0°, 2.6 g. IIIa and 3.4 g. IIIb; in boiling C6H6, 6.2 g. IIIa and 0.7 g. IIIb. By heating in C6H6 IIIb is converted largely into IIIa. The corresponding acid (IVa) (from IIIa) m. 157° (decomposition) (from MeCN or AcOEt); IVb (from IIIb), m. 139° (decomposition). Heating IIIa with MeOH, gives the mono-Me ester of IVa, m. 124°, which with CH2N2 forms the di-Me ester (Va), m. 66° (from Et2O). With Busch-Stove's catalyst (C.A. 10, 2727) Va adds H, giving the corresponding dihydro derivative, m. 114° (from AcOEt). Va (2 g.) refluxed with 2 g. Na in 40 cc. MeOH, followed by addition of H2O, further refluxing, washing with Et2O, acidification, and extraction with AcOEt gave (in poor yield) the corresponding trans acid (VIa), m. 206°, (decomposition), complete hydrogenation of which with PtO2 gave the dihydro derivative (VIIa) of VIa, m. 205°, giving a sharp m.-p. depression when mixed with VIa. IIIa shake n 48 hrs. with 50% H2SO4 gave the cis lactone (VIIIa), m. 202° (from AcOEt); dihydro derivative (IXa) of VIIIa, m. 176°. Me ester (Xa) of VIIIa, m. 156° (from ligroin). The trans lactone (XIa), m. 171° (from AcOEt), was formed by treating Xa with MeONa; dihydro derivative of XIa, m. 176-8° (showing a sharp m.-p. depression when mixed with IXa). Xa adds PhN3, forming a compound (not analyzed), m. 209°, not identical with the (unanalyzed) hydrotriazole, m. 214° (obtained from PhN3 and IIIa), which in aqueous NaOH, followed by cooling and addition of AcOH, gave the phenyliminodicarboxylic acid (XII), m. 184° (from aqueous MeOH); di-Me ester of XII, m. 143° (from Et2O). In the above reaction if XII was not filtered but treated with AcOH until solution occurred, followed by addition of H2O and concentration in vacuo, there was formed a lactone monocarboxylic acid, m. 223° (from aqueous MeOH), whose mono-Me ester, C19H2104N, m. 227° (from MeOH). Partial reduction of IIIa with Pd-CaCO3 in AcOEt gave a dihydro derivative (XIII), C12H1403, m. 138° (from ligroin); corresponding free acid, m. 184° (from AcOEt), with loss of H2O; mono-Me ester, m. 138°; di-Me ester, m. 108° (from Et2O), yielding, with MeONa, a trans acid (XIIIa), m. 171°; this on hydrogenation gave VIIa, m. 205°. The mother liquors from VIIa probably contained another (impure) saturated acid (probably identical with XVI described below). XIII in aqueous Na2CO3 with 4% KMnO4, after extraction with H2O, filtration, and acidification of the filtrate, gave the alc. (XIV); Me ester, m. 150° (from ligroin-AcOEt). (In one such oxidation the reaction also gave small amts. of Me2CO.) XIII

L6 ANSWER 76 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
with 30% H2O2 in glacial AcOH and H2SO4 or with O3 in aq. NaOH gave, after extn. with Et2O and acidification, a compd. (XV), m. 252°; Me ester, m. 201° (from MeOH). The Na salt of XIII and NaOBr at 0°, followed by acidification, gave the Br analog of XV, m. 202° (from AcOEt); Me ester, C13H17O4Br, m. 141° (from MeOH). Further hydrogenation of XIII in AcOH with PtO2 gave an impure product, m. 101°, still showing unsatn. This, on oxidation with alk. KMnO4, conversion to the free acid, and treatment with AcCl, yielded the tetrahydro deriv. of IIIa, C12H16O3, m. 107-8° (from ligroin). The mono-Me ester of the corresponding dibasic acid, m. 112°, gave a di-Me ester (not isolated) which was converted with MeONa and hydrolysis into the trans acid (XVI), m. 208-9° (from AcOH) (giving a sharp m.-p. depression with VIIa). IIIb with PhN3 in AcOEt gave a hydrotriazole m. 203°, not identical with that obtained from IIIa. PtO2 and H acting on IIIb in AcOEt gave a dihydro deriv., C12H14O3 (XVII), m. 172°, adding MeOH to give the mono-Me ester (of the corresponding dibasic acid), m. 116° (from AcOEt), giving with CH2N2 a di-Me ester, m. 41° (from Et2O), which was converted into XIIIa, m. 172°. Ozonization of XVII in AcOH gave 80% of the theoretical yield of Me2CO. XVII with PtO2 and H gave 2 tetrahydro derivs., C12H16O3, of IIIb; a less sol. isomer, m. 107°, and a more sol. isomer, m. 80° (both from ligroin). These, on sapon. and hydrolysis gave the resp. cis acids (XVIII), m. 196°, and (XIX), m. 178°. XVIII was rearranged into the trans isomer, XVI. XIX on trans rearrangement gave VIIa. With (.tplbond.CCO2Me)2 under N, I gave the adduct C14H16O4, m. 101° (from MeOH), which with colloidal Pd in MeOH gave a dihydro deriv. (XX), m. 64-5° (from MeOH). Complete hydrogenation with PtO2 gave an unidentified oil. p-Benzoquinone and I in EtOH gave the adduct, C14H14O2, m. 118°. I and H2C : CHCN (after 6 weeks at room temp.) gave an (unanalyzed) adduct, m. 86-90°. Pentamethylenefulvene and II in Et2O at 0° (and subsequent standing at room temp.) gave the adduct "A" (XXI), C15H16O3, m. about 148° (depending on the rate of heating) (cf. Kohler and Kable, C.A. 29, 4334.7, who give 132°); the Et2O mother liquors from XXI gave on very slow evapn. the isomeric adduct B (XXII), m. 96° (from ligroin). The mother liquors from XXII were also carefully evapd. to dryness, treated with concd. aq. Na2CO3, and the resulting Na salt converted into the free acid (corresponding to XXII), C15H18O4, m. 137° (from ligroin). The over-all yield of XXI, XXII, and the acid was 74% of the theoretical. When heated in C6H6, XXII was recovered unchanged, whereas XXI was largely isomerized into XXII. XXI is the endo-adduct and XXII the exo-adduct. XXI added PhN3, giving the hydrotriazole, C21H21O3N3, m. 220° (from AcOEt) (decompn.). Hydrogenation with Busch-Stove catalyst gave a dihydro deriv. of XXI, m. 145°, yielding the dibasic cis-acid, m. 160° (decompn.) (from MeCN), the di-Me ester of which (not identified) was isomerized and hydrolyzed to the trans acid (XXIII), m. 229° (from AcOEt). XXII forms a hydrotriazole, C21H21O3N3, m. 191° (decompn.) (from AcOEt). When shaken with 50% H2SO4, XXII formed a lactone acid, C15H18O4, m. 204-5° (analogous to VIIIa); mono-Me ester, m. 112° (from petr. ether). The latter heated with PhN3 in AcOEt evolved N, yielding the Me ester of a phenylimino lactonic acid, C22H25O4N, m. 194°. The dihydro deriv. of XXII m. 106°; corresponding free acid (XXIV) m. 138° (decompn.), trans isomerization of which gave XXIII. XXIV adds HOBr at room temp. giving a bromo lactone acid, C15H19O4Br, leaflets, m. 167-8° (from aq. AcOH); mono-Me ester, C16H21O4Br, m. 133° (from MeOH).

IT 107-13-1, Acrylonitrile
(reaction with 6,6-dimethylfulvene)

L6 ANSWER 76 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)

L6 ANSWER 77 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1948:8243 CAPLUS
DOCUMENT NUMBER: 42:8243
ORIGINAL REFERENCE NO.: 42:1793e-h
TITLE: Mechanism of catalytic hydrogenation and dehydrogenation with rhodium
AUTHOR(S): Hernandez, L.; Nord, F. F.
CORPORATE SOURCE: Fordham Univ., New York, NY
SOURCE: Experientia (1947), 3, 489-490
CODEN: EXPEAM; ISSN: 0014-4754
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB A Rh catalyst prepared with polyvinyl alc. as a supporting colloid differs from similarly prepared Pd catalysts (cf. C.A. 35, 7810.7) in being sensitive to pH and to the presence of functional groups. E.g., the values of the reaction velocity constant, k + 106, are at room temperature 11.1, 10.8, 10.4, 10.1, 9.25, 9.02, 8.79, 6.25, and 1.85 for the hydrogenation of nitrobenzene parasubstituted with CN, CHO, NO2, COOH, I, Cl, Br, OCH3, and NH2 groups, resp., whereas the value for nitrobenzene is 8.33. Furthermore, for the Pd catalyst the value of k + 106 is 18.5 for nitrobenzene with or without the above list of p-substituted groups. For the hydrogenation of C:C in allylamine, acrylic acid, acrylonitrile, allyl alc., allyl acetate, allyl ethyl ether, and acrolein, the values of k + 105 for the Rh catalyst are 3.12, 2.63, 2.12, 2.08, 1.94, 0.97, and 0.28, resp. The authors conclude that Rh ionizes the H so that H+ is the effective hydrogenating agent, whereas for Pd, H atoms are involved. The authors also find that S enhances the activity of the Rh catalyst toward the dehydrogenation of formic acid and isopropyl alc. at 95°.

IT 107-13-1, Acrylonitrile
(hydrogenation on Rh, kinetics of)

RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)

L6 ANSWER 78 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1947:9953 CAPLUS
DOCUMENT NUMBER: 41:9953
ORIGINAL REFERENCE NO.: 41:2074e-i
TITLE: Amino ethers
PATENT ASSIGNEE(S): Wingfoot Corp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 581994		19461031	GB	

AB Compds. having the formula NH2CH2C(X)HCH2OR, where X is Me, Et, or H, and R is an aliphatic group which may contain the ether, amino, and HO radicals, are obtainable by hydrogenating the nitriles resulting from the reaction between polyhydric alcs. and acrylonitrile (I), methacrylonitrile, or ethylacrylonitrile in the presence of alkaline catalysts. Thus O(CH2CH2OH)2 (II) 318, I 318, and NaOMe 2 g. gave 2,2'-bis(2-cyanoethoxy)diethyl ether, b8-14 227-38°, nD27 1.4478, d1528 1.067, which on reduction with H at 1000 lb./sq. in. in the presence of Raney Ni at 125-40° gave 2,2'-bis(3-aminopropoxy)-diethyl ether. With 1 mol. I and 1 mol. II, 2-(2-cyanoethoxy)-2'-hydroxydiethyl ether, b9 186°, nD22 1.4452, d1532 1.089, was obtained which gave 2-(3-aminopropoxy)-2'-hydroxydiethyl ether on hydrogenation. Glycerol (III) (1 mole) and 2 moles I give a mixture of 1,3-bis(2-cyanoethoxy)-2-hydroxypropane and 1,2-bis(2-cyanoethoxy)-3-hydroxypropane which hydrogenate to 1,3-bis(2-aminoethoxy)-2-hydroxypropane and 1,2-bis(2-aminoethoxy)-3-hydroxypropane. With 1 mole I and 1 mole III a mixture of 1,2-dihydroxy-3-(2-cyanoethoxy)propane and 1,3-dihydroxy-2-(2-cyanoethoxy)propane is formed which gives on reduction 1,2-dihydroxy-3-(3-aminopropoxy)propane and 1,3-dihydroxy-2-(3-aminopropoxy)propane. With 3 mols. I and 1 mole III 1,2,3-tris(2-cyanoethoxy)propane is formed, giving on hydrogenation 1,2,3-tris(3-aminopropoxy)propane, 1,3-bis(3-aminopropoxy)-2-hydroxypropane, 1,2-bis(3-aminopropoxy)-3-hydroxypropane, and PrNH2. With 2 moles I and 1 mole 2,3-butanediol (IV), 2,3-bis(2-cyanoethoxy)butane is obtained; with 1 mole of each, 1-hydroxy-3-(2-cyanoethoxy) butane and 1-(2-cyanoethoxy)-3-hydroxybutane are obtained. By hydrogenation , 2,3-bis(3-aminopropoxy)-, 2-(3-aminopropoxy)-3-hydroxy-, 1-hydroxy-3-(3-aminopropoxy)-, 1-(3-aminopropoxy)-3-hydroxy-, and 1,3-bis(3-aminopropoxy)butane are obtained. From 2-methyl-2,4-pentanediol and I, 2-methyl-2,4-bis(3-aminopropoxy)-, 2-methyl-2-(3-aminopropoxy)-4-hydroxy-, and 2-methyl-2-hydroxy-4-(3-aminopropoxy)pentane are obtainable. Cf. C.A. 39, 4624.1.

IT 1647-11-6, Butyronitrile, 2-methylene-
(and reaction products with polyhydric alcs., hydrogenation of)

RN 1647-11-6 CAPLUS
CN Butanenitrile, 2-methylene- (9CI) (CA INDEX NAME)

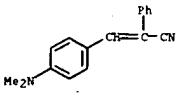
IT 107-13-1, Acrylonitrile

L6 ANSWER 78 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
(reaction products with polyhydric alcs., hydrogenation of)
RN 107-13-1 CAPLUS
CN 2-Propenenitrile (CA INDEX NAME)

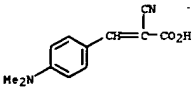
IT 126-98-7, Methacrylonitrile
(reactions of, with polyhydric alcs., hydrogenation of)
RN 126-98-7 CAPLUS
CN 2-Propenenitrile, 2-methyl- (CA INDEX NAME)

L6 ANSWER 79 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN
ACCESSION NUMBER: 1932:20813 CAPLUS
DOCUMENT NUMBER: 26:20813
ORIGINAL REFERENCE NO.: 26:2185c-i,2186a-b
TITLE: p-Dimethylaminobenzal ketones. II. Auxochromic groups
AUTHOR(S): Rupe, H.; Collin, August; Sigg, Walter
SOURCE: Helvetica Chimica Acta (1931), 14, 1355-69
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB These investigations indicate that the NMe2 group acts strongly to deepen color in unsatd. ketones, especially in mols. having the group -CO.CH:CH-. The diphenylhexatriene of Kuhn and Winterstein (C. A. 22, 1767) is yellow while 1-phenyl-7-(p-dimethylaminophenyl)-1,3,6- heptatrien-5-one (I) is red and their diphenyloctatetraene is greenish chrome-yellow while 1-phenyl-9-(p-dimethylaminophenyl)-1,3,5,8-nonatetraen-7-one (II) is vermilion. α-Phenyl-p-dimethylaminocinnamonitrile, Me2NC6H4CH:C(CN)Ph (III), obtained by the method of Kauffmann (C. A. 11, 2805), intensely yellow with bright yellowish green fluorescence, m. 136°; HCl salt, white, m. 184-8° (decomposition); acid sulfate; perchlorate, decomps. 164-70°; methiodide, m. 185°; methosulfate, C19H22O4N2S, m. 261°; 60% H2SO4 hydrolyzes the nitrile to the corresponding acid, yellowish brown needles, m. 223°. (Me2NC6H4CH2CHPhCH2)2NH (IV), obtained in 6 g. yield from 40 g. III by hydrogenation in 500 cc. EtOH and AcOH mixture with 40 g. Ni catalyst at 100 atms. and 40-50°, m. 107°; picrolonate, brownish yellow prisms, m. 207°. Another secondary amine isomeric with IV, possibly the meso-form, is obtained in 4 g. yield from the reaction producing IV, m. 85° (mixed m. p. with IV, 92-6°); phenylthiourea derivative, m. 166°. The primary amine Me2NC6H4CH2CHPhCH2NH2 is obtained in 9 g. yield from the reaction which produces IV, yellow oil, b13 225-9°, which on standing forms a nearly colorless crystal cake; phenylthiourea derivative, m.
147°; picrolonate, citron-yellow, m. 222°.
p-Dimethylaminobenzaldesoxybenzoin ketimide, Me2NC6H4CH:CPh:NH (V), obtained by adding 10 g. III to 31 g. PhBr and 5 g. Mg in C6H6, warming 4 hrs. on the water bath and extracting with ether after adding water, bright yellow, m. 150°, dissolves in dilute acids with blood-red color, dyes mordanted cotton red and unmordanted cotton dirty yellow. Hydrolysis of V with 20% boiling HCl for 0.5 hr. yields p-dimethylaminobenzaldesoxybenzoin. yellow, m. 167°, soluble in HCl without color and identical with the compound of Kauffmann (C. A. 11, 2794). Et α-cyano-p-dimethylaminocinnamate (VI), obtained by warming equivalent amts. of Me2NC6H4CHO and NCCH2CO2Et in alc. with NaOH, orange-yellow, m. 122°; perchlorate, pale yellow; methosulfate, pale yellow m. 197°. Me2SO4 also forms an addition product with Me2NC6H4CH:CHCOMe, m. 202°, easily hydrogenated.
α-Cyano-p-dimethylaminocinnamic acid, obtained by warming VI on the water bath with 30% NaOH until the orange color becomes pale yellow, orange- red, m. 212°. Longer treatment of VI with NaOH gives Me2NC6H4CHO. α-Dimethylaminobenzyl-β-aminopropionic acid, obtained by hydrogenating at 80 atms. and 40-50° for 5 hrs. 20 g. VI in 250 cc. alc., 250 cc. AcOH and 50 cc. water with 60 g. Ni catalyst, and hydrolyzing the yellow oil formed with HCl, m. 235°; the Cu salt was prepared and analyzed; 2 g. dissolved in water and heated to dryness with 2 g. KCNO and then to dryness with 20% HCl and taken up with water gave a white precipitate with NaOH,
crystallizing from alc., m. 237°, of 5-dimethylaminobenzylhydrouracil. I was obtained by warming 40 g.

L6 ANSWER 79 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
Me2NC6H4CH:CHCOMe in 300 cc. alc. with 28 g. PhCH:CHCHO and NaOH at 40°, intensely red, m. 150°; HCl salt, green and unstable; methiodide, paleocher-colored crystals from MeOH, m. 175°. Phenylbutyl p-(dimethylaminophenyl)- ethyl ketone, obtained in 25 min. by hydrogenating 20 g. I in 250 cc. alc., 250 cc. AcOEt and 50 cc. water with 20 g. Ni catalyst and the theoretical vol. of H for the 3 double bonds (4.75 l.), purifying the yellow oil formed after removal of solvents by crystn. of the semicarbazone, and recovering the ketone by warming with oxalic acid, b0.05 172-5°, pale yellow oil becoming red on standing, forms a colorless soln. in HCl; semicarbazone, m. 105°. II was obtained by warming 20 g. Me2NC6H4CH: CHCOMe in 150 cc. alc. with 17 g. of the phenylpentadienal of Vorl.acte.ander (C. A. 23, 3687) and NaOH, vermilion, m. 184°. Phenylhexyl p-(dimethylaminophenyl)ethyl ketone, obtained by hydrogenating 20 g. II in 500 cc. alc. and 50 cc. water with 20 g. Ni catalyst and 5.85 l. H at 60°, and purifying the yellow oil by crystn. of the oxalate from alc. since the semicarbazone did not form, pale yellow oil, b0.1 187°, setting to a colorless crystal mass, m. 27-8°; oxalate, m. 105°.
IT 1222-61-3, Acrylonitrile, β-(p-dimethylaminophenyl)-α-phenyl-
(and derivs.)
RN 1222-61-3 CAPLUS
CN Benzeneacetonitrile, α-[[4-(dimethylamino)phenyl]methylene]- (9CI) (CA INDEX NAME)



IT 57711-73-6P, Cinnamic acid, α-cyano-p-dimethylamino-
860737-69-5P, Ammonium, [p-(β-carboxy-β-cyanovinyl)phenyl]trimethyl-, methylsulfate
RL: PREP (Preparation)
(preparation of)
RN 57711-73-6 CAPLUS
CN 2-Propenoic acid, 2-cyano-3-[4-(dimethylamino)phenyl]- (9CI) (CA INDEX NAME)



RN 860737-69-5 CAPLUS
CN Ammonium, [p-(β-carboxy-β-cyanovinyl)phenyl]trimethyl-, methylsulfate (3CI) (CA INDEX NAME)

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L6 ANSWER 79 OF 79 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
CRN 860737-68-4
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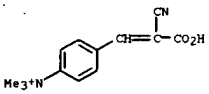
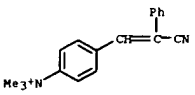


CM 2

CRN 21228-90-0
CMF C H3 O4 S

IT 802333-08-0, Ammonium, [p-(β-cyanostyryl)phenyl]trimethyl-
(salts)
RN 802333-08-0 CAPLUS
CN Ammonium, [p-(β-cyanostyryl)phenyl]trimethyl- (8CI) (CA INDEX NAME)



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Inventor Name Search Result

Your Search was:

Last Name = VEDAGE
First Name = GAMINI

Application#	Patent#	Status	Date Filed	Title	Inventor Name
06500037	4480131	150	06/01/1983	PROCESS FOR SELECTIVE PRODUCTION OF DI- AND TRI-ALKYLAMINES	VEDAGE, GAMINI A.
06555579	4642381	150	11/28/1983	CATALYST AND METHOD FOR PRODUCTION OF METHYLAMINES	VEDAGE, GAMINI A.
06912882	4766247	150	09/26/1986	COLOR REDUCTION OF POLYAMINES BY MILD CATALYTIC HYDROGENATION	VEDAGE, GAMINI A.
07175010	Not Issued	163	03/30/1988	CATALYTIC HYDROGENATION OF CRUDE METHYLENE BRIDGED POLYPHENYLAMINES TO PRODUCE POLYCYCLOHEXYLAMINES	VEDAGE, GAMINI A.
07175444	4960941	150	03/30/1988	HYDROGENATION OF AROMATIC AMINES TO PRODUCE THEIR RING HYDROGENATED COUNTERPARTS	VEDAGE, GAMINI A.
07175551	Not Issued	163	03/31/1988	CRUDE METHYLENEDIANILINE HYDROGENATION	VEDAGE, GAMINI A.
07336184	5026914	150	04/11/1989	HYDROGENATION OF AROMATIC AMINES USING RHODIUM ON TITANIA OR ZIRCONIA SUPPORT	VEDAGE, GAMINI A.
07699425	5196587	150	05/13/1991	CATALYTIC HYDROGENATION OF CRUDE METHYLENE BRIDGED POLYPHENYLAMINES TO PRODUCE POLYCYCLOHEXYLAMINES	VEDAGE, GAMINI A.
07743463	5264501	250	08/09/1991	ALKYL SUBSTITUTED BI (CYCLOHEXYLAMINES)	VEDAGE, GAMINI A.
07852602	Not Issued	163	03/17/1992	PROCESS FOR HYDROGENATION OF ORTHO-TOLIDINE TO ALKYL SUBSTITUTED BI	VEDAGE, GAMINI A.

				(CYCLOHEXYLAMINES)	
08040311	6121493	150	03/30/1993	ISOMERIZATION OF CYCLOHEXYLAMINES TO PRODUCE THEIR THERMODYNAMIC ISOMERIC FORM	VEDAGE, GAMINI A.
08043646	6140540	150	04/06/1993	HYDROGENATION OF AROMATIC AMINES TO PRODUCE THEIR RING HYDROGENATED COUNTERPARTS	VEDAGE, GAMINI A.
08083843	5360934	150	06/25/1993	HYDROGENATION OF AROMATIC AMINES TO PRODUCE THEIR RING HYDROGENATED COUNTERPARTS	VEDAGE, GAMINI A.
08092042	5288424	250	07/15/1993	ALKYL SUBSTITUTED BI (CYCLOHEXYLAMINES)	VEDAGE, GAMINI A.
08127659	5973207	150	09/27/1993	HYDROGENATION OF META-TOLUENEDIAMINE	VEDAGE, GAMINI A.
08179466	5444170	150	01/10/1994	HYDROGENATION OF ACETYLENIC COMPOUNDS	VEDAGE, GAMINI A.
08306069	5545756	150	09/14/1994	HYDROGENATION OF AROMATIC AMINES USING MIXED METAL OXIDE SUPPORT	VEDAGE, GAMINI A.
08382739	5574189	150	02/02/1995	HYDROGENATION OF NITRILES TO PRODUCE AMINES	VEDAGE, GAMINI A.
08393145	5567847	150	02/21/1995	DISPROPORTIONATION OF AMINES TO PRODUCE SECONDARY AMINES	VEDAGE, GAMINI A.
08564666	5639916	150	11/29/1995	AMINATION OF ALLYLIC ALCOHOLS	VEDAGE, GAMINI A.
08631280	5672762	150	04/12/1996	HYDROGENATION OF NITRILES TO TERTIARY AMINES	VEDAGE, GAMINI A.
09130936	6005143	150	08/07/1998	USE OF A MONOLITH CATALYST FOR THE HYDROGENATION OF DINITROTOLUENE TO TOLUENEDIAMINE	VEDAGE, GAMINI ANANDA
09561071	6184416	150	04/28/2000	Lithium aluminate as a catalyst support for hydrogenation of aromatic amines	VEDAGE, GAMINI ANANDA
10051934	6429338	150	01/17/2002	HYDROGENATION OF SINGLE RING AROMATIC DIAMINES	VEDAGE, GAMINI ANANDA
10313560	6774264	150	12/06/2002	CATALYST TO IMPROVE THE COLOUR STABILITY OF N,N-DIALKYLALKANOLAMINES	VEDAGE, GAMINI ANANDA

10359450	6962964	150	02/06/2003	HYDROGENATION OF METHYLENEDIANILINE HOMOLOGS AND EPOXY RESINS CURED WITH SAME	VEDAGE, GAMINI ANANDA
10634516	7009081	150	08/04/2003	N-METHYLATED AMINES FROM SELECTIVE VAPOR PHASE AMINATION OF AMINO ETHER ALCOHOLS	VEDAGE, GAMINI ANANDA
10655145	Not Issued	30	09/04/2003	Aminopropylation of alcohols in the presence of amide or ether solvents	VEDAGE, GAMINI ANANDA
10848766	7038088	150	05/19/2004	HYDROGENATION OF HIGHLY CONTAMINATED METHYLENEDIANILINE	VEDAGE, GAMINI ANANDA
10925105	6998507	150	08/24/2004	HYDROGENATION OF METHYLENEDIANILINE	VEDAGE, GAMINI ANANDA
11233439	Not Issued	71	09/22/2005	Hydrogenation of aromatic amines to alicyclic amines using a lithium aluminate-based catalyst	VEDAGE, GAMINI ANANDA
11418288	Not Issued	30	05/04/2006	Trimer catalyst additives for improving foam processability	VEDAGE, GAMINI ANANDA
11450834	Not Issued	30	06/09/2006	Polyamide curing agent compositions	VEDAGE, GAMINI ANANDA
11582178	Not Issued	20	10/17/2006	Crosslinkers for improving stability of polyurethane foams	VEDAGE, GAMINI ANANDA
11584388	Not Issued	30	10/20/2006	Curing agent for low temperature cure applications	VEDAGE, GAMINI ANANDA
11598415	Not Issued	30	11/13/2006	Use of a polyamine stream as curing agent in epoxy adhesive and flooring applications	VEDAGE, GAMINI ANANDA
11672298	Not Issued	30	02/07/2007	Alkylated Polyalkyleneamines and Uses Thereof	VEDAGE, GAMINI ANANDA
11672994	Not Issued	30	02/09/2007	Polyamide Curing Agent Compositions	VEDAGE, GAMINI ANANDA
11673697	Not Issued	30	02/12/2007	Selective Manufacture of N,N'-BIS (Cyanoethyl)-1,2-Ethylenediamine and N, N'-BIS(3-aminopropyl)-1,2-Ethylenediamine	VEDAGE, GAMINI ANANDA
11740307	Not Issued	16	04/26/2007	New Amine Composition	VEDAGE, GAMINI ANANDA

08958894	5886227	250	10/28/1997	PROCESS FOR HYDROGENATION OF CYANOPROPIONALDEHYDE-CONTAINING CYANOPROPIONADELHYDE ACETALS	VEDAGE, GAMINI ANANDA
09013624	5932769	150	01/26/1998	MULTI-METALLIC CATALYSTS FOR AMINATION OF ALCOHOLS TO FORM ALKYLAMINES	VEDAGE, GAMINI ANANDA
09049540	5917092	150	03/27/1998	METAL EXCHANGED ZEOLITE CATALYSTS FOR ALCOHOL AMINATION	VEDAGE, GAMINI ANANDA

Inventor Search Completed: No Records to Display.

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Inventor Name Search Result

Your Search was:

Last Name = LUTZ
First Name = EUGENE

Application#	Patent#	Status	Date Filed	Title	Inventor Name
60721692	Not Issued	159	09/29/2005	Bag-holder and lid	LUTZ, EUGENE D.
60852097	Not Issued	20	10/16/2006	Hand-held bag holder	LUTZ, EUGENE D.
06144805	4284837	150	04/29/1980	PROCESS FOR RECOVERY OF AN ALIPHATIC DIOL OLIGOMERIZATION SOLVENT	LUTZ, EUGENE F.
06221955	4317938	150	12/31/1980	PREPARATION OF SECONDARY ALKANOL ALKOXYLATES	LUTZ, EUGENE F.
06267169	Not Issued	161	05/26/1981	PROCESS FOR MAKING CERTAIN DIEPOXIDES	LUTZ, EUGENE F.
06308631	4404406	150	10/05/1981	OXIDATION OF ISOBUTANE UNDER SUPER-CRITICAL CONDITIONS	LUTZ, EUGENE F.
06337232	Not Issued	164	01/06/1982	COMPLEXING ACID RECOVERY	LUTZ, EUGENE F.
06363175	4474678	150	03/29/1982	ALKANOL ETHOXYLATE-CONTAINING DETERGENT COMPOSITIONS	LUTZ, EUGENE F.
06435429	4423256	150	10/20/1982	RECOVERY OF SECONDARY ALKANOLS	LUTZ, EUGENE F.
06441830	4443418	150	11/15/1982	METHOD OF REMOVING HYDROGEN SULFIDE AND CARBON DIOXIDE FROM GASER	LUTZ, EUGENE F.
06569423	4502538	150	01/09/1984	POLYALKOXY SULFONATE, C02 AND BRINE DRIVE PROCESS FOR OIL RECOVERY	LUTZ, EUGENE F.
06658949	4528416	150	10/09/1984	ETHYLENE OLIGOMERIZATION PROCESS CARRIED OUT IN A MONOHYDRIC/ DIHYDRIC	LUTZ, EUGENE F.

				ALCOHOL SOLVENT MIXTURE	
06659207	Not Issued	161	10/09/1984	ETHYLENE OLIGOMERIZATION PROCESS	LUTZ, EUGENE F.
06673646	Not Issued	161	11/21/1984	SULFONATE SURFACTANT COMPOSITION AND A METHOD FOR ITS PREPARATION	LUTZ, EUGENE F.
06853508	Not Issued	166	04/18/1986	PROCESS FOR THE PREPARATION OF SULFONATE SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
06943355	H000479	150	12/19/1986	WOOD PULP BLEACHING PROCESS	LUTZ, EUGENE F.
07102764	Not Issued	161	09/24/1987	PROCESS FOR THE PREPARATION OF SULFONATE SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07230808	Not Issued	166	08/09/1988	PROCESS FOR THE PREPARATION OF SURFACTANTS HAVING IMPROVED PHYSICAL PROPERTIES	LUTZ, EUGENE F.
07545025	5075041	250	06/28/1990	PROCESS FOR THE PREPARATION OF SECONDARY ALCOHOL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07622208	Not Issued	161	11/30/1990	PROCESS FOR THE PREPARATION OF SURFACTANTS HAVING IMPROVED PHYSICAL PROPERTIES	LUTZ, EUGENE F.
07718031	Not Issued	161	06/20/1991	PROCESS FOR THE PREPARATION OF SURFACTANTS HAVING IMPROVED PHYSICAL PROPERTIES	LUTZ, EUGENE F.
07890056	Not Issued	161	05/28/1992	SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07946120	5281366	250	09/17/1992	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT	LUTZ, EUGENE F.

				COMPOSITIONS	
07951955	5250718	250	09/28/1992	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07974658	5290484	250	11/12/1992	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07980887	Not Issued	166	11/24/1992	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07990920	Not Issued	166	12/15/1992	SECONDARY ALKYL SULFATE/ZEOLITE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
07994022	5349101	250	12/21/1992	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
08100659	Not Issued	161	07/30/1993	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
08197370	Not Issued	161	02/16/1994	PROCESS FOR THE PREPARATION OF SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
08198677	5427717	150	02/18/1994	SECONDARY ALKYL SULFATE/ZEOLITE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.
08208157	Not Issued	161	03/08/1994	SECONDARY ALKYL SULFATE-CONTAINING SURFACTANT COMPOSITIONS	LUTZ, EUGENE F.

08618179	5672802	150	03/19/1996	PROCESS FOR THE PREPARATION OF ALPHA OLEFINS	LUTZ, EUGENE F.
11689252	Not Issued	25	03/21/2007	OLEFIN CONVERSION PROCESS AND OLEFIN RECOVERY PROCESS	LUTZ, EUGENE FREDERICK
60785340	Not Issued	159	03/23/2006	Olefin conversion process and olefin recovery process	LUTZ, EUGENE FREDERICK
07089293	4873315	150	08/25/1987	PERFLUORINATED PROPYL DERIVATIVE COMPOUNDS	LUTZ, EUGENE G.
07313129	4925992	150	02/21/1989	PERFLUORINATED-2-ISOPROPYL DERIVATIVE COMPOUNDS	LUTZ, EUGENE G.
07329122	4901910	150	03/27/1989	PERFLUORINATED PROPYL DERIVATIVE COMPOUNDS FOR VAPOR BATH SOLDERING	LUTZ, EUGENE G.
10655145	Not Issued	30	09/04/2003	Aminopropylation of alcohols in the presence of amide or ether solvents	LUTZ, EUGENE GEORGE
11233439	Not Issued	71	09/22/2005	Hydrogenation of aromatic amines to alicyclic amines using a lithium aluminate-based catalyst	LUTZ, EUGENE GEORGE
11673697	Not Issued	30	02/12/2007	Selective Manufacture of N,N'-BIS(Cyanoethyl)-1,2-Ethylenediamine and N, N'-BIS (3-aminopropyl)-1,2-Ethylenediamine	LUTZ, EUGENE GEORGE
11740307	Not Issued	16	04/26/2007	New Amine Composition	LUTZ, EUGENE GEORGE
09327656	6060624	150	06/08/1999	RACEMIZATION OF OPTICALLY ACTIVE ALKOXYAMINES	LUTZ, EUGENE GEORGE

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Application#	Patent#	Status	Date Filed	Title	Inventor Name
10655145	Not Issued	30	09/04/2003	Aminopropylation of alcohols in the presence of amide or ether solvents	ENGEL, MATTHEW J.
11233439	Not Issued	71	09/22/2005	Hydrogenation of aromatic amines to alicyclic amines using a lithium aluminate-based catalyst	ENGEL, MATTHEW J.
09997328	Not Issued	161	11/29/2001	Method and apparatus for alleviating pain	ENGELBERT, MATTHEW T.
10352352	Not Issued	161	01/27/2003	Leach-field water level monitoring system	ENGELMAN, MATTHEW R.
60359712	Not Issued	159	02/27/2002	Passive air injection system for pumped septic wastewater effluent	ENGELMAN, MATTHEW R.
60359713	Not Issued	159	02/27/2002	Leachfield wastewater monitoring system	ENGELMAN, MATTHEW R.

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